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Physics in the Textile Industry

THE broad field of opportunity for physicists in industrial research is strikingly illustrated in the four papers in this issue on the applications of physics in the textile industry, which were given recently in a symposium which was a part of the joint meeting of the American Physical Society and the American Association of Physics Teachers, at Chapel Hill, N. C. The present state of development and the magnitude of the textile industry offer almost limitless possibilities for good fundamental research.

The method of attack of the physicist, in this instance, is characteristic. He tries to discover the fundamental structure of the fibers that go to make up cotton threads. He realizes that these fibers differ in form, length and breaking strength. The physicist recognizes that variations in the individual fibers influence the quality of the cloth in a statistical manner. Further, to complete his studies, he must know how the properties of the individual fibers vary from a given mean. It is only then that he can hope to predict, after the complete shuffling which these fibers undergo in being formed into a piece of cloth, the physical properties of the final product.

The physicist's interest and abilities in this work extend in many other directions. He investigates the effects of moisture in cotton and develops instruments for the accurate measurement and control of the relative humidity during the processing of the cloth. His fundamental studies of the fiber structure, combined with a knowledge of the effect of moisture, lead to possible solutions of the shrinkage problem. Still another important contact exists for the physicist in the textile industry; for instance, in the specification and control of color. This all important question falls very naturally in his field since only by spectral reflectance relations can one describe completely the color of a piece of cloth.

The service of the physicist in this field is just starting. We wish him the greatest success. In the words of Mr. Elting, "When such studies find themselves full-fledged and in common use, the manufacture of cotton textiles may be elevated from the state of an art to that of a science."

—THE EDITOR

For May

National Bureau of Standards, by LYMAN J. BRIGGS

Uses and Limitations of X-Ray Diffraction Methods, by JOHN T. NORTON

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Minute Nonferritic Particles in Steel, by A. B. KINSEL

Contributed Research Papers on the Filtering Action of Porous Media, Heat Effects in Capillary Flow at High Rates of Shear, and Effects of Pressure and Temperature on the Viscosity of Lubricating Oils.

Structure of the Cotton Fiber*

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ALTHOUGH current scientific journals have published no statements to this effect, it is quite certain that there are biologists in all parts of the world who now pause frequently in remembrance of important discoveries which were being made just one hundred years ago. The botanical researches of Schleiden in Jena and the zoological researches of Schwann in Berlin were summarized in 1837 with the simple statement that *all organized bodies are composed of essentially similar parts, namely cells.* It is particularly fitting, therefore, that these scientists should be mentioned in connection with a description of the structure of the cotton fiber, a highly specialized plant cell.

The unit structure to which they referred is in itself quite complicated. Many of its physical and chemical constituents are not identifiable by any existing techniques. With suitable magnification we may readily discern, however, the viscous *cytoplasm* which forms the basic material, the dense *nucleus* which is suspended in it, and the *cell membrane* which surrounds it. In the formation and functioning of these three primary components, the basic principles which are responsible for life itself are involved. Their differential development brings about an almost endless variety of cellular forms. In the mature cotton fiber the cell membrane reaches such a state of over-development that the material of which it is composed makes up all but a few percent of the entire mass of the cell. The fibers vary greatly in length and diameter and in the relative proportions of length to diameter. It is not at all unusual, however, for a fiber whose average diameter is 1/1000 of an inch to attain a length equal to 2000 times this width. A cross section of a fiber shows that two-thirds or more of the thickness is made up of cell membrane material.

In the study of the microscopic structure of many kinds of plant and animal cells it is frequently advantageous to cover the entire period of development as well as the mature state. This method of approach has proved to be unusually helpful in learning more of the fine structure of the cell membrane of the cotton fiber. We have long known that it is made up largely of cellulose; that the cellulose is elaborated in the living cytoplasm; and that it is deposited in relatively enormous quantities to form the cell membrane.[1] It has been the current belief that cellulose itself cannot be found in the living cytoplasm before the membrane is formed. Its chemical and optical identification has been confined, therefore, to cell membrane material.

A careful microscopic examination of an actively growing cotton fiber reveals the fact that this belief is unfounded. Cellulose in the form of small ellipsoid particles is scattered throughout the viscous living mass.[2] These particles have been observed in various types of plant cells, which were engaged in cellulose membrane formation, for the past century. They have played an important part in producing the frequently described "granular" appearance of the cytoplasm. Previous identification of their chemical nature had failed because of the presence upon the surface of the *cellulose particles* of a material which reacts positively to neither the optical nor the microchemical tests for cellulose.

In our present state of knowledge it is impossible to think of the cellulose particle as completely dissociated from this surface coating. When we remove the particles from the young cell for closer scrutiny, its presence is clearly

* Presented at the American Physical Society Symposium on Physics in the Textile Industry held February 19–20, at Chapel Hill, North Carolina.

evidenced by their staining reactions, their dullness which approaches invisibility when unstained, and their delayed reaction to microchemical tests for cellulose. If, through washing the particles with weak acids or alkalies, we dissolve away enough of the protective coating to alter their staining behavior, greatly increase their brightness, and render almost instantaneous their reaction to microchemical tests for cellulose, we still cannot be certain that we have completely removed the coating. Many of its properties are similar to those of the viscous colloidal phase of the cytoplasm in which the particles are suspended. It may be nothing more than an adhering layer of this mixture whose chemical complexities are themselves not understood. In any event, the close physical relationship between the cellulose reacting portion of the particle and the comparatively thin colloidal coating is maintained during the later stages of membrane formation which follow. In this process the coating takes on the added role of a *cementing material* which holds the particles together. In disintegrating the mature membrane for the purpose of again separating the particles this cementing material is partially, if not completely, removed. It is necessary, therefore, in our present state of knowledge and technical skill, that the cellulose particle taken from the living cytoplasm represent the physical unit upon which measurements of its specific properties are based.

One of the most impressive properties of a mass of particles is their uniformity in size. This is observable only when they are in an even focal plane. The degree of magnification needed to bring them into clear relief is near to one thousand diameters. Within the short focal distances involved, there is still a wide variation in the sharpness of focus of the different particles in any given field. Apparent differences in size often result from these variations in the sharpness and are not real. The approximate length of a single particle as it exists in the living cell is 1.5 microns. This measurement is believed to be very nearly correct since it is possible to check it with the average length per particle in chains of varying numbers of particles arranged end to end. Their orientation in the chain is not difficult to observe since the particles are definitely ellipsoid. The length of the short axis is not so easily determined and may be verified only through comparison with the long axis, since, in the cotton fiber, the associated particles are always in single rows, end to end, and not side

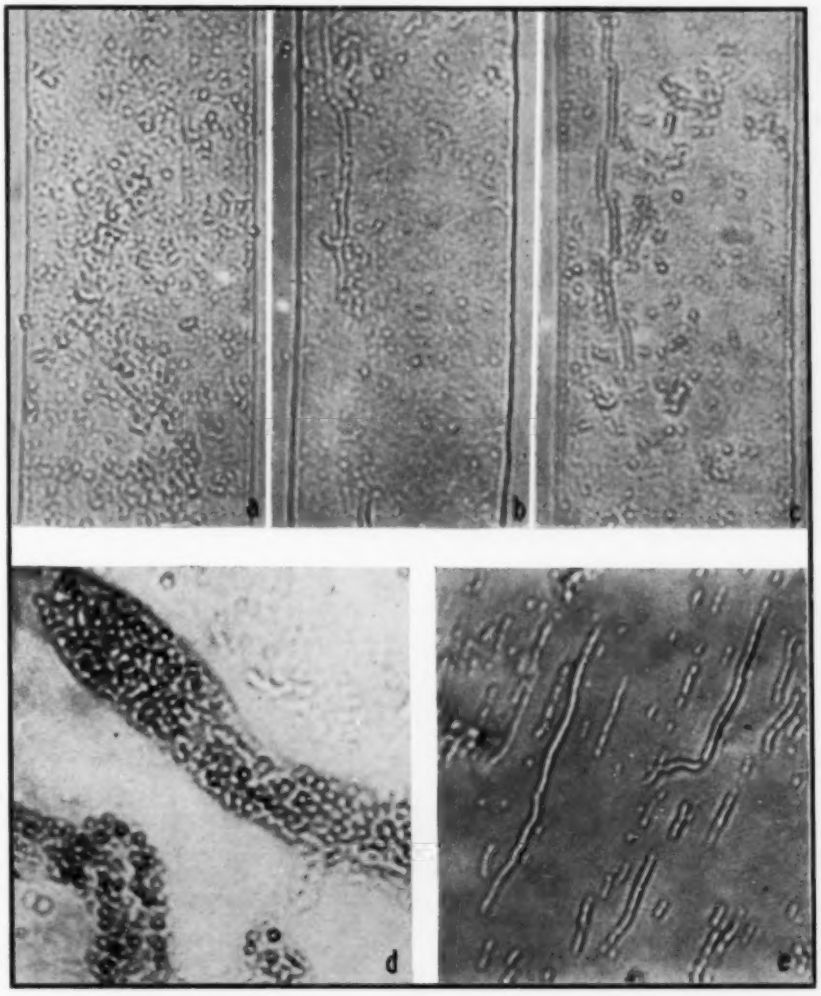

FIG. 1. *a*, *b*, *c*. Cellulose particles and fibril formation in the cytoplasm of the young cotton fiber; *d*, the "sulphuric acid-iodine" reaction of particles from the living cytoplasm; *e*, fibrils and particles dissected from a developing membrane.

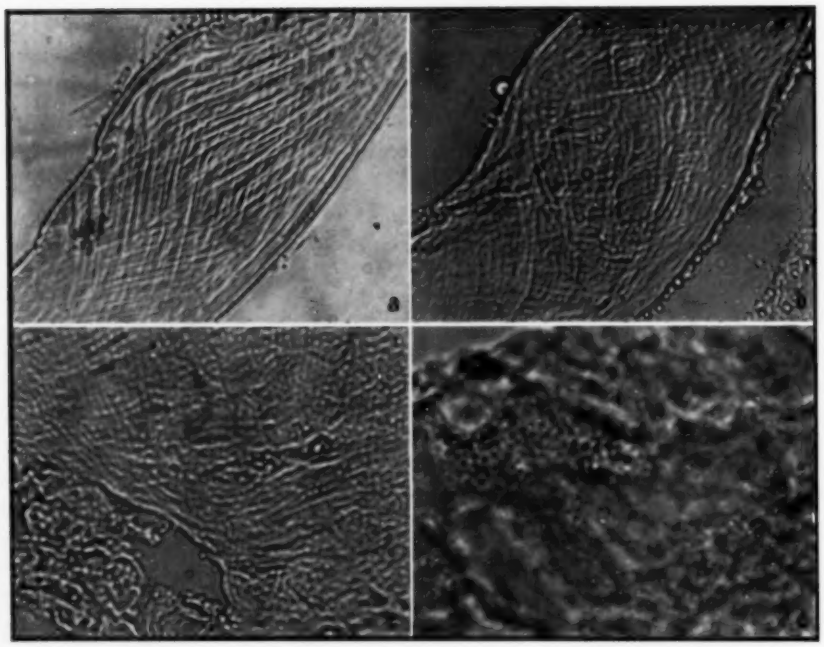

FIG. 2. *a*, *b*, *c*. Disintegration of membrane of mature cotton fiber into fibrils and cellulose particles; *d*, a mature cotton fiber after treatment with phosphoric acid and iodine shows blue coloration of the hydrolyzing particles surrounded by the uncolored cementing material.

by side. The value which seems to be most nearly accurate for the length of the shorter axis is 1.1 microns. It must be pointed out that all measurements of a structure of this size and composition under the necessary optical conditions is difficult and is, at best, an approximation. It is hoped that particles from disintegrated mature membranes may later furnish material for extensive measurements of a more specific nature. The accumulation of such data must follow and not precede final improvements in the technique of the removal of cementing material. A closer approach to absolute values for size than is represented in the present approximations must depend upon increased skill in many lines of technique other than direct measurement.

Cellulose particles from young cotton fibers were likewise used for measurements of the refractive indices. In order to obtain values more nearly representative of the cellulose portion of the particle, the surface coating was at least partially removed by means of a suitable solvent. Since at least one of the constituents of this colloidal material is pectic, any one of the ordinary pectic solvents is effective for this purpose. In this particular instance ammonium hydroxide was used, the treated mass of particles was washed with water and dried at room temperature before proceeding with the measurements. Since the particles are doubly refractive, the highest and lowest indices are at the positions of extinction in polarized light with Nicols crossed. These positions were determined, the upper Nicol removed and the respective indices determined by the immersion method. For the single particles as well as for the rows of particles these indices are 1.565 lengthwise and 1.530 crosswise.

Microscopic observations have shown that particles are not only present in the cytoplasm at the earliest stage of fiber elongation, but that formation of the membrane from these particles begins soon thereafter. X-ray diffraction patterns of masses of particles from very young cotton fibers have recently added further evidence as to the cellulose nature of the particles in the living cytoplasm. Removal of the waxes and the colloidal materials serve to sharpen the cellulose lines in the pattern so that they can be definitely identified.[3]

One of the most useful techniques in demonstrating the cellulose nature of the particles is the sulphuric acid-iodine test. The hydrolytic swelling of the particle is accompanied by a clear blue coloration in the presence of iodine. If sufficient iodine is added to the mount to more than satisfy the absorptive properties of the surrounding materials, the particle upon the addition of the sulphuric acid reacts with the free iodine in the fashion long recognized to be characteristic of cellulose. If sufficient care is used in applying this test, the successive stages of hydrolysis may be observed and readily photographed, due to the color change in the particle. If the acid used is too strong, the reaction is almost instantaneous, and the color reaction very temporary. If sufficient iodine is not present, swelling of the particle occurs but

no coloration. The value of this test depends solely upon the precision with which it is used.

The cellulose nature of the particle is even more firmly established by its behavior during the actual membrane formation. In the central regions of the cytoplasm the particles are separate or in very short rows. In the outer regions the rows are much longer. In these long rows the particles finally become so closely appressed that the microscopic identity of the particles themselves is lost in the formation of the *cellulose fibril*. These fibrils are fastened upon the original limiting membrane of the fiber by means of the cementing material which coats them. The final arrangement in the wall is that of an irregular spiral with frequent reversals and a tendency to reverse the direction in the successive layers. In the basal regions of some of the young fibers the typical crossed spiral arrangement of the fibrils is already in evidence.

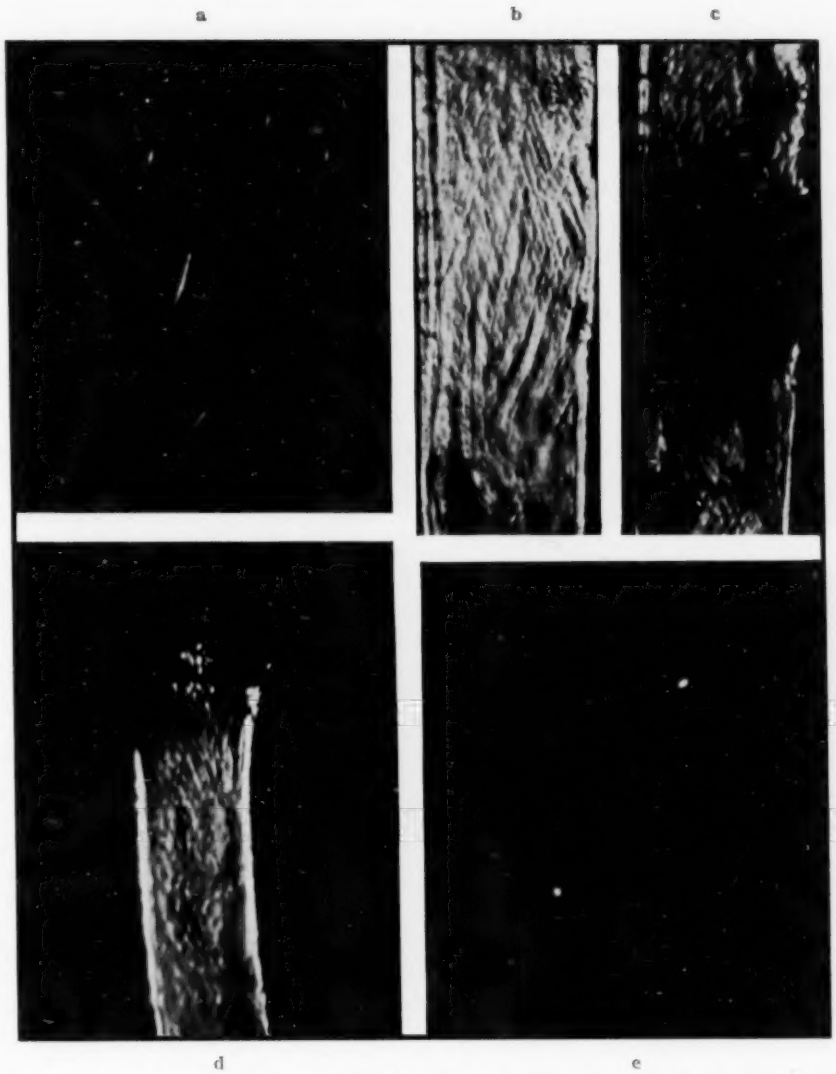

FIG. 3. In polarized light. *a*, Strands of cellulose particles in cytoplasm of living cotton fiber; *b*, spiral fibrils of mature fiber in position of brightness; *c*, extinction of fibrils and cellulose particles in mature fiber in area in which their long axes are parallel to the direction of the beam; *d*, mature fiber disintegrating into fibrils and particles; *e*, single particles.

The illustrations shown and the remarks concerning them are from our own experimental data. It gives me unusual pleasure, however, to summarize these remarks with a quotation from Valentin[4] written at the close of his study of plant cell membrane formation in 1837: "In the youngest cells there exists a simple cell enveloping membrane without any indication of fibrils. There is stored in the interior of the cell a fine granular mass. The tiny particles have at first no regular arrangement. Later they build lines, in which one, early in the development, may still distinguish the particles and which finally form an unbroken continuity."

During the period of membrane development the fibers within the boll are moist and the membranes may be disintegrated into fibrils and particles through mechanical action alone. After the onset of desiccation which begins before the opening of the boll the cementing material of the membrane is more resistant to pressure or grinding action alone and "solvents" must be employed. The list of agents with which the membrane of the mature fiber may be disintegrated into fibrils and particles is long. Their action may now be studied from the standpoints of the specific reactions of cellulose particles and cementing material. The variability of the reactions is thus greatly increased. Our work in this field has only begun. While it is impossible

to mention all of the types of differential behavior observed, a few instances will serve to illustrate the general importance of such results.[5]

When mature cotton fibers are treated with weak solutions of certain acids or alkalies, a very gradual disintegration of the membrane takes place. After a long period of time with repeated extractions the separation into fibrils and the fibrils in turn into particles is accomplished. The process may be followed microscopically as layer upon layer of the membrane is removed. Cross sections of fibers in which the cementing material has been swollen but not destroyed show the alternate concentric layers of swollen cementing material and cellulose. In such a cross section whose diameter when unswollen is 25 microns the number of layers of cellulose is 12. From the filtrates in which masses of fibers have been treated at least certain components of the cementing material may be recovered by precipitation. One of these has been definitely identified as pectic acid.[6] Microscopic, microchemical, and x-ray diffraction analyses show no change in the cellulose reactions of the particles which remain.

In strong hydrochloric acid (sp. gr. 1.19) the cementing material is broken down and removed from the membrane complex so that the separated particles are freed. Our various techniques confirm the identity of these cellulose particles with those observed during cell membrane formation.[7, 8] If hydrolysis of any of the cellulose occurs, it is slight. The addition of iodine produces no blue coloration. In sulphuric acid (50–75 percent) the cementing material is removed and the particles rapidly hydrolyzed. A blue coloration with iodine results from this hydrolysis. Both of these acid treatments have the disadvantage microscopically of removing the cementing material. The differential reaction of the two membrane components could be best demonstrated with both in evidence. In phosphoric acid we more nearly approach this ideal condition. A compound is formed with the cementing material and the cellulose reacting portion of the particles is hydrolyzed. When iodine is added to a microscopic mount of fibers so treated, the swelling and blue coloration of the particles is clearly discernible in the presence of the swollen, transparent, cementing material.

As a result of these separations of the cellulose membrane into two physically distinct components which have been seen but not fully recognized for the past hundred years, our research has taken a new trend. One of its immediate objectives is the complete separation and recovery of the cellulose particles and the cementing material for more detailed chemical, physical and microscopic analyses. In the course of these studies the physical relationships which exist between the particle and the substance which surrounds it as well as the physical reactions of the separated constituents will hold a place of equal importance with the chemical behavior. Nature makes possible these methods of procedure by differentiating from the other constituents of the living cytoplasm the cellulose to be used for membrane construction in the form of units which maintain their identity through a surprisingly large number of manipulations.

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The Physical Basis of Color Measurement*

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A HOUSEHOLD word like *color* would seem to require no definition. Its meaning is learned during infancy and is not easily forgotten. In fact, only scientists have difficulty in defining the term, the difficulty resulting chiefly from their innate desire to restrict every term to a single meaning. In this instance, scientists are not in good agreement among themselves with respect to the meaning that should be adopted. One group, consisting largely of chemists, uses *color* as a generic term for dyes, pigments, and similar materials. Physicists generally associate color with the spectral distribution of radiant energy in the visible region of the spectrum. A third group, comprising most physiologists and psychologists, attempts to define color as a sensation in the brain of a human observer. These three uses of the term are so different that one group has great difficulty in understanding the other two.

Ordinarily a physicist is more interested in procedures employed to measure color than he is in the results of the measurement. This is entirely compatible with his instincts, which have always taught him to attempt the measurement of every property that an object or material may possess. When he embarks on theoretical excursions, they are usually interludes for the purpose of interpreting measurements that do not agree with the predictions of existing theories. With these instincts and traditions, he has been led to adopt a very rational attitude in the matter of definitions. Instead of defining a quantity and then attempting to discover some means of measuring it, he first establishes a mensurational procedure and then associates a name with the quantity thus evaluated. As a result, the definition of every physical property is expressed in terms of the operations employed in the mensurational procedure. The definition of color is no exception. To learn what a physicist means by color, one has merely to ascertain the steps that a physicist employs to measure color.

The color measurements which a physicist makes are often misunderstood by those who fail to realize that there are few objects or materials that can be regarded as possessing a single color in the ordinary sense of the word. The color of glossy samples in particular depends to a great extent on the direction from which the light falls on them and the direction from which they are viewed. Even samples that are nearly devoid of gloss show some variation in color with the mode of illumination and observation. A physicist often encounters situations like this. He knows, for example, that the diameter of a piece of wire is influenced by such factors as the temperature of the wire and the stress to which it may be subjected. The customary expedient in such cases is to include with the results a statement concerning the conditions under which the tests were conducted. Unfortunately, this does not always protect him in the field of color measurement. If he measures the color of a test sample under various modes of illumination and observation and then reports all his results, he exposes himself to the charge that his results do not agree among themselves. If he makes only one measurement, his result may be criticized by anyone who customarily examines colored materials under some different mode of illumination or observation. The chemical definition of color is undoubtedly responsible for this state of affairs. A dyer in a textile mill,

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for example, believes with much justification that the color of the finished goods depends primarily on the formula of the dye bath. In a chemical sense he is entirely correct. In an optical sense he is wrong, as even a cursory examination of a glossy material will demonstrate.

There are an infinite number of ways in which a sample can be illuminated, and there are also an infinite number of ways in which it can be viewed. Due to the impracticability of realizing all of these modes of illumination and observation, physicists have generally confined themselves to two limiting cases which have been

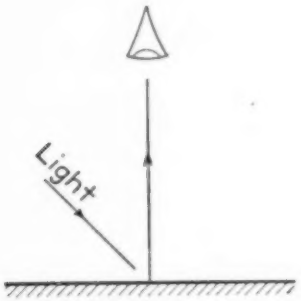

FIG. 1.

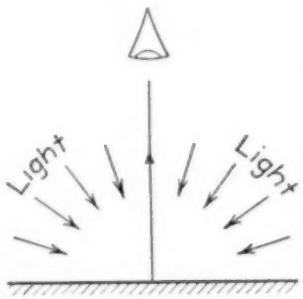

FIG. 2.

employed more widely than any others. One is represented diagrammatically in Fig. 1. In this case, a nearly unidirectional beam of light is incident on the sample at an angle of 45 degrees, the sample being viewed along the normal to its surface. This mode corresponds rather closely to observing the sample under direct sunlight or under the light from any single source. The other common mode is illustrated in Fig. 2. In this case, light is incident upon the sample from all angles, the direction of viewing being again along the normal to the surface. This mode corresponds to observation of the sample out-of-doors on a completely overcast day. It would be out of place here to present arguments in favor of either of these modes.[1] In fact, the choice of modes cannot be made on logical grounds but only on the basis of expediency and convenience. Suffice it to conclude, therefore, that every attempt to measure color must be preceded by a decision with respect to the mode of illumination and observation that is to be adopted. After the measurements are made, the results will have no significance unless the mode of illumination and observation is stated.

The physical operations employed in the measurement of color become straightforward as soon as the mode of illumination and observation has been selected. The fundamental instrument for this purpose is a spectrophotometer.[2] In comparison with the complicated processes that are stimulated in the human eye during the ordinary visual inspection of colored materials, spectrophotometric observations are exceedingly simple. Referring again to Fig. 1, let it be assumed that the light incident on the sample consists of a narrow spectral band, such as might be isolated from the light of a tungsten lamp by the aid of a monochromator. When illuminated in this manner all samples, regardless of their color, will differ only in relative brightness. It therefore becomes a simple matter to insert an ordinary brightness photometer between the sample and the eye, and by this means to determine the brightness of one sample relative to that of another sample. The second sample may conveniently be a surface that has been freshly smoked with magnesium oxide. Not only is such a surface very reproducible, but it reflects so nearly all the light incident upon it that it has been commonly adopted as the white standard for all reflection measurements.[3]

The nature of the results obtained with a spectrophotometer and one reason for their importance can best be illustrated by reciting a short chapter from the traditions of the institution with which the author is associated. In 1876, the freshman class at the Massachusetts Institute of Technology appointed a committee to consider the matter of a college color. This

[1] It is always possible to interchange the source of light and the observer. That is, diffuse illumination and normal observation (Fig. 2) yield the same results as normal illumination and diffuse observation. Both diffuse illumination and diffuse observation are usually effected by the use of integrating spheres.

[2] Spectrophotometers are frequently employed in the comparison of light sources and in the measurement of the color of transparent materials. In this discussion, the test sample will be assumed to be opaque, since opaque samples are of greater importance numerically.

[3] Absolute methods of reflectometry have been devised which are independent of any material standard. These methods would undoubtedly be more widely used if magnesium oxide standards were not so satisfactory.

committee recommended cardinal and silver gray, and these colors were first used as the official Institute colors at the prize drill in May, 1876. During the course of the next fifty years, the Institute colors evidently became progressively duller. In fact, the Alumni Council in 1926, at the instance of some of the older alumni, appointed a committee to standardize the two colors. After much search, this committee discovered in the archives of the Alumni Association two pieces of remarkably fresh-looking and well documented silk ribbon which dated back to the earlier period. In another vault the committee found some ribbon that had been dyed to a subjective color match in 1905. Since the 1905 specimens matched the originals rather well, it was decided to standardize the 1905 specimens rather than to take the chance of accidental injury to the irreplaceable originals.

With the two samples selected, it was a simple matter to make the necessary spectrophotometric measurements. One at a time, the brightness of each sample was compared with that of a fresh surface of magnesium oxide under the same illumination, both sample and standard being illuminated diffusely and observed normally. Observations were made at wave-length intervals of 10 millimicrons throughout the visible region, the wave-length band in each case being so narrow that the use of a narrower band produced no significant change in the results. These tests were made first at the National Bureau of Standards and were subsequently checked in our own laboratory, with a spectrophotometer of a somewhat different type. The actual standardization of the colors was made on the basis of the recorded data but, for ready visualization, the data are represented graphically in Fig. 3. The ordinates in this case are labeled "reflectance," it being understood that the reflectance is relative to that of magnesium oxide. The abscissae represent the wave-length of the light in millimicrons. With this information preserved in several depositories, it is unthinkable that the M. I. T. colors could ever be lost.

This example, although of sentimental rather than commercial value, may serve to illustrate the basic nature of spectrophotometric measurements. The results depend only on determinations of the wave-length and relative quantities of light, assuming that either an absolute method or a reproducible white standard is used. The results are not in the least affected by the character of the light source or by the visual processes of the observer. In fact, the eye of the observer can frequently be replaced to advantage by a photoelectric cell, provided precautions are taken to insure that the results will be independent of the cell characteristics.

The importance of this ability to measure colors in such a manner that the results will be

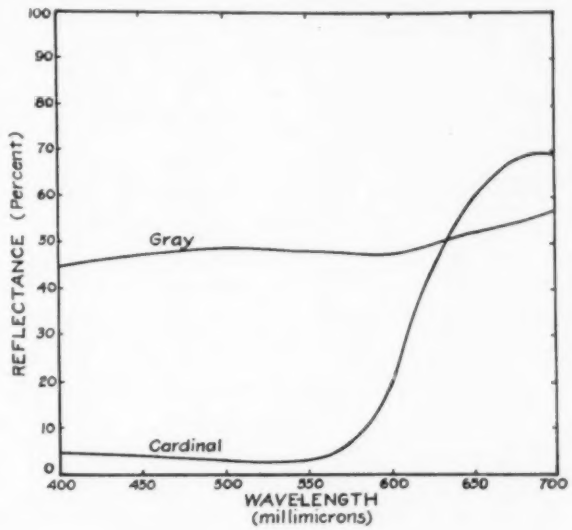

FIG. 3.

intelligible at any future time can scarcely be overemphasized. There are thousands of persons engaged daily in the production or application of colored materials who, without spectrophotometry or some method having its roots in spectrophotometry, are unable to keep satisfactory records of their efforts. It has been said that man's superiority to the lower animals is due primarily to the fact that he invented a language which enabled him to share information with his contemporaries and to record his observations for the use of future generations. Spectrophotometry may very properly be regarded as the first and basic language of color.

But for the fact that people sometimes look at colors, a physicist would have no need to carry his investigations beyond this point. In fact, if the human eye had been endowed with the analytical ability of the human ear, the concepts of spectrophotometry would be intuitive and

the remainder of this discussion would be unnecessary. As it is, a spectrophotometer supplies much more information than the unaided eye is able to acquire. This information is almost always useful, but in one case it is a source of embarrassment. Consider the two spectrophotometric curves shown in Fig. 4. Both samples are an almost perfect visual match by daylight, yet they have very different spectrophotometric characteristics. That they really are different is easily demonstrated by changing the illuminant. Under tungsten light, Sample A is definitely green and Sample B is a purplish blue. Although this behavior is readily explained qualitatively by reference to the two curves, it is not so easy to see that both samples would be the same blue under daylight.

The accepted method of proving that two things are alike is to show that both are equal to something else. In this case, use is made of a long-established principle that any color stimulus can be matched visually by a mixture of three primary color stimuli. Suppose it is determined in some suitable manner that Sample A can be matched by X parts of one primary, Y parts of the second primary, and Z parts of the third. Suppose further that Sample B can be matched visually by X' parts of the first primary, Y' parts of the second, and Z' parts of the third. Then, if $X'=X$, $Y'=Y$, and $Z'=Z$, it is clear that Samples A and B must be a visual color match under the assumed conditions. The choice of primaries is evidently unimportant, since they merely provide the means of making the comparison.

The procedure employed in the evaluation of X, Y and Z, is briefly as follows. If Sample A is illuminated by daylight, the spectral quality of the light entering the eye of an observer will be the spectral quality of daylight modified by the reflection characteristics of the sample. It is thus a simple matter to determine by computation the relative energy distribution of the light entering the eye of an observer. This light is heterogeneous; and it simplifies the problem to consider it wave-length by wave-length, especially since each wave-length affects the eye in a different manner.

The most reliable data concerning the effect of homogeneous radiant energy on the normal human eye were determined independently by Wright and by Guild in England about 1928. In effect, these investigators determined at convenient wave-length intervals (10 millicrons) throughout the visible spectrum the amounts of three arbitrarily selected primaries that are required to color match a unit amount of homogeneous radiant power of the several wave-lengths. Many observers cooperated in these determinations, so many in fact that the use of a larger group would not be expected to produce significant changes in their findings. Although Wright and Guild employed different primaries,

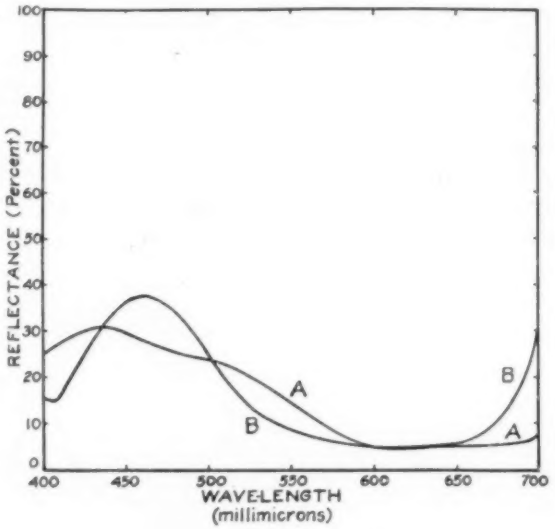

FIG. 4.

their results were found to be in excellent agreement when reduced to the same basis. They were also found to be in substantial agreement with previous data, about which there had been some uncertainties. When the International Commission on Illumination met in 1931, these data of Wright and Guild were adopted as representative of the response of a normal observer to a unit amount of homogeneous radiant power at the specified wave-lengths.

With this information available, it is a straightforward computational procedure to determine how much of the I. C. I. primaries would be required by the I. C. I. observer to color match a given sample under daylight illumination, or under any source whose spectral distribution is known. Since the amount of energy entering the eye in any wave-length band can be readily

calculated, it is but a simple step to find how much of each primary would be required to color match the light in this band. By totaling the amounts for all the bands into which the visible spectrum has been divided, the values of X, Y and Z are obtained.

The computational procedure outlined above, although perfectly straightforward, is often tedious. There have therefore been many attempts to construct instruments known as colorimeters that will determine the values of X, Y and Z directly. A typical form of such an instrument contains a photometric cube in the observer's field of view. One-half of the field is filled by light reflected from the test sample when it is illuminated in the desired manner. The other half of the field is filled by a mixture of lights from the three primary sources in controlled amounts. By manipulation of the three controls, the observer is able to find a unique setting for which the two halves of the field are an exact color match. The readings of the three controls are then an indication of the amounts of these primaries required by this observer to color match the test specimen. If desired, the results can be transformed to indicate the amounts of the I. C. I. primaries[4] that would have been required by the I. C. I. observer, provided the actual observer has strictly normal color vision. Since the energy distributions in the two halves of the photometric are often very different, slight departures from normalcy on the part of the observer have a pronounced effect on the results. The precision requirements in colorimetric measurements are ordinarily so severe that, for inter-laboratory comparisons or for long-range standardization programs, many observers must cooperate in each determination. For this reason it is usually simpler to determine the spectrophotometric characteristics of the sample and then to determine by computation the three tristimulus values that the I. C. I. observer would obtain if he were to use a colorimeter employing the I. C. I. primaries.

There have been many attempts in recent years to construct colorimeters in which the eye of the observer is replaced by a photoelectric cell and a set of three filters. Obviously, if the variations in the visual response among normal individuals are so great as to discourage the use of colorimeters, much development work must be done on photoelectric cells and filters before photoelectric colorimeters will earn the right to use the term *colorimeter*. Unless the three filter-cell combinations simulate rigorously the chromatic properties of the normal human eye, the readings of the instrument will give the tristimulus values for some individual who has probably never existed and whose opinions on the subject of color are of slight concern. These remarks are not intended to disparage the use of such instruments in their proper sphere. With their faults corrected, they could become colorimeters; with their faults uncorrected, they can be used for abridged spectrophotometry. In the latter case, it is advantageous to use as many filters as the art of making band-pass filters permits. Used in this way, the spectral sensitivity characteristics of the cells become progressively less important as the width of the spectral bands is decreased. In the limit these characteristics are of no consequence, but then the instrument becomes a spectrophotometer.

As indicated previously, it is frequently desirable to determine tristimulus values in order that subjective color matches under daylight, or under some other assumed source, may be recognized. It is also useful, in the preservation of data, to file in the same place all information pertaining to colors that look alike under the standard illuminant, even when the colors are spectrophotometrically very unlike. For these and for many other purposes there is another language, derivable from the tristimulus language, which has all of its advantages and the additional advantage of easy visualization. Just as any color stimulus can be matched by a mixture of three primaries, it can also be matched by a mixture of white light and homogeneous light of the proper wave-length. In other words, if a test sample has tristimulus values X, Y, Z, a mixture of white light and homogeneous light of some wave-length can be found that will have the same tristimulus values and will therefore be a subjective match. The wave-length of the homogeneous light is called the *dominant wave-length* of the sample. The *brightness* of the

[4] The I. C. I. primaries are unrealizable experimentally. They were so chosen because to do so simplifies their use in computation.

sample is the sum of the brightnesses of the two components. The *purity* of the sample is measured by the proportion of the homogeneous light in the mixture; homogeneous light of every wave-length having a purity of 100 percent, white light having a purity of zero. In these terms, the M. I. T. colors under daylight can be designated as follows:

	Brightness	Dominant Wave-Length	Purity
Cardinal	10.1%	620 mμ	63.9%
Gray	48.3%	576 mμ	1.5%

The cardinal is seen to be a moderately dark color associated most closely with that point in the red region of the spectrum where the wave-length is 620 millimicrons. The high purity shows it to be a rather strong or saturated red. The gray is really a moderately light yellow. Its purity is so low, however, that it evidently departs but little from a true neutral gray.

The promulgation and universal adoption of the findings of the 1931 International Commission on Illumination complete the last chapter in the development of methods of color measurement and specification. Although some further improvements in instruments are to be expected as a matter of course, it seems probable that these improvements will merely facilitate the obtaining of data without altering the basic principles of colorimetry. The next step is the application of the methods of colorimetry to the scientific study of diverse color phenomena and to the routine problems of industry.

As an example of the former, it is possible at the present time to ascertain by measurement and computation that two colors would look alike to a normal observer under some standard illuminant. If it happens that they would not look alike, it is ordinarily impossible to specify the degree of their difference in terms of the color difference that a normal observer could just perceive. The determination of just perceptible differences for a large gamut of colors under a wide variety of observing conditions is a task whose magnitude dwarfs the development of the science of colorimetry. Nevertheless, it is an investigation that can profitably be undertaken, now that an imperishable language of color has been devised.

It would be incorrect to imply that all the remaining problems are of an experimental nature. Some of them can be attacked theoretically, the type of attack savoring strongly of the methods of thermodynamics. The recent work of MacAdam may be cited as an example in this connection. Starting with the premise that no surface can, at any wave-length, have a reflectance greater than 100 percent or less than zero, MacAdam undertook to determine what colors are theoretically obtainable assuming unlimited freedom in the choice of spectrophotometric characteristics. His results assign a value to the maximum brightness of a colored surface having any specified dominant wave-length and purity. By reference to these results, anyone engaged in the production of new colors may determine in advance the directions in which progress is possible and the directions in which experiments are foredoomed to failure. As a guide for research programs, such information is invaluable.

The applications of colorimetry by industry, although increasing constantly, are still in their infancy. The strained economic conditions of the last few years have not produced the auspicious circumstances that a new born technique requires for rapid growth. Another handicap is the specious argument that color measurements are unnecessary because nature has endowed us with sense organs adaptable to this purpose. This argument may be challenged on logical grounds because the human eye cannot be said to measure anything in the ordinary sense of the word *measure*. From the standpoint of industries that are beginning to wonder about the possible uses of colorimetry, it is sometimes more effective to allude to other physical measurements that are made everyday in competition with our sensations, For example, such fundamental quantities as mass, length, time, and temperature have long since been evaluated objectively instead of being estimated subjectively. In the field of acoustics, which is closer of kin to optics, physical concepts and physical measurements are almost invariably employed. This list of examples might be extended, but it is unnecessary to do so because everyone who has observed the rapid growth of mass production methods in industry realizes that these methods require accurate color control. In other words, the color of all the peas in the pod must be the same also.

The Place of Statistics in Textile Research*

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THE textile industry is very old, much older than the theory of mathematical probability which was formulated about two hundred years ago. This industry which has existed in some form for centuries continues to exist today somewhat as an art. That statistical methods are not in general use today is due largely to the fact that their introduction requires the joint effort of many men over long periods of time. The failure to adopt statistical methods more rapidly is not the fault of the industry itself, but rather is due essentially to the difficulty of teaching an old dog new tricks. The introduction of statistical methods in the textile industry is quite analogous to convincing a small boy of the benefits of taking castor oil. The ultimate advantages are neither obvious nor immediately tangible. The treatment, however, is well tested, and we know that it produced good results for the neighbor's boy.

The newer industries, created within the last century and untrammeled by tradition, have grown up with the development of the theories of probability. They have, therefore, been in a position to take advantage of these methods from the very outset. Modern industrial methods are inextricably interwoven with statistical problems.

Scientific research in the field of textiles is itself a development of very recent years. In fundamental scientific research statistical methods have been and are being used generally and need no further discussion here. This paper deals with those phases of the use of statistics in research and manufacture which concern the control of the product.

The incentives for the application of statistical methods to practical textile problems coming as they do largely from research are frequently thought to be very *experimental* or *theoretical* by the uninformed. The introduction of these methods into the textile industry is at present experimental only in the limited sense that the introduction of any sort of new method into any industry is necessarily experimental during the early stages of application.

Statistics, or more specifically, the mathematics of probability, which is essentially the body of principles for determining the qualities of large parent groups from limited amounts of data, finds most valuable application where large quantities of material are involved. Where then can statistics be of greater usefulness than in the cotton textile industry where, as we shall see, many million different items may be assembled each second in one small mill.

The United States produces an annual cotton crop of about 14 million bales. These bales weigh about 500 pounds each. In every pound of this cotton there are approximately 140 million cotton fibers.[1] This annual crop, therefore, amounts to the staggering figure of roughly a million million million cotton fibers, or the number 1 followed by eighteen ciphers.

If these million million million fibers were all spun into a single 30s yarn, a very common size of thread, this thread would be approximately 100,000 million miles long, or the number 1 followed by eleven ciphers. For those who are astronomically minded, a conception of this length may be had from the fact that the yarn would be long enough to go more than five and a half times around the orbit of Neptune. The mean distance from the sun to Neptune is about

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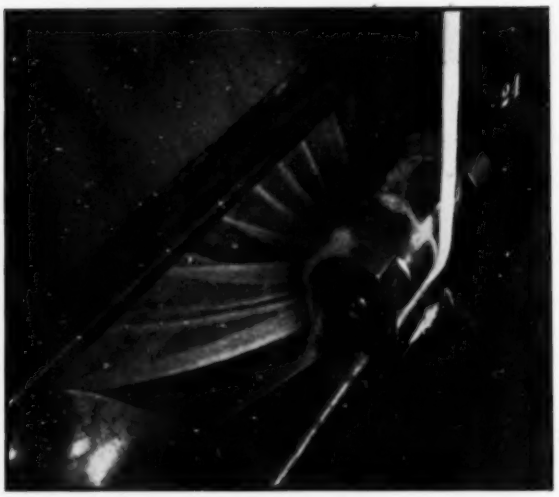

FIG. 1. Cotton leaving a card. For the first time after the cleaning and opening operations, the cotton fibers are brought together at this point to form a rope-like strand known as a sliver.

2,800 million miles. For those of us who feel somewhat more at home on the earth, this length of yarn could be wrapped around the equator approximately 4 million times.

The cotton textile industry is concerned not only with vast numbers of minute fibers, but also with the fact that these fibers differ widely in their physical properties. For example, the cotton fibers vary greatly in length, cross-sectional area and shape, maturity, twist, etc. Photomicrographs showing these properties may be found in the work of Schwarz,[2, 3] Farr, Clark,[4] Matthews,[1] and others. The tensile strength of these fibers also varies widely, but in general has a magnitude between that of cast iron and very mild steel. The breaking strength of common American types is generally between 50,000 and 70,000 pounds per square inch of cross section.[5] Sea Island cotton may be even stronger.

One of the most strikingly apparent, as well as one of the most important, variable physical properties of cotton is that of fiber length. To the textile industry and to the cotton broker, cotton is 15/16 of an inch, 1 inch, or $1\frac{1}{16}$ inches long, as the case may be. Actually, however, the individual fibers in samples so classed may vary from almost immeasurably short hairs to hairs one and a half to two inches in length. Each cotton fiber is thus an individual in a population. Just as the individuals in a crowd of people viewed from an airplane appear to be identical, with the possible exception of a few bald pates which may glisten in the sun, so are the cotton fibers identical when viewed in a mass. However, when one comes closer to the group of people, or to the group of cotton fibers, each person or fiber begins to show its individuality, different in some respect from every other. Some are tall and some are short; some thick and some thin; some strong and others weak. It is rather apparent that each cotton fiber is an individual and the cotton as a whole must be considered as a population of which the physical characteristics vary widely.

Wherever such large and varied populations exist it is insufficient to select any one individual as representative of the group. Rather, one must determine the likelihood or probability that the other individuals will not differ from this individual by more than a specified amount. Thus, one may obtain distribution curves characteristic of the physical properties of the cotton fibers making up a population. These curves portray the nature of the parent group and are, in some cases, very similar to the theoretical error curve. It is perhaps from this point that the application of statistics to the cotton textile industry begins. The phenomena which are observed in the textile mill are the result, not of the behavior of any single fiber or machine, but of the characteristics of the entire population of fibers and of the entire group of machines.

In the production of a yarn the millions of fibers must be shuffled much as one shuffles a deck of cards. In the final yarn there is, therefore, a more or less random distribution of the fibers having different physical properties. But again, as with playing cards, shuffling does not eliminate the possibility of the occurrence of either exceedingly good or exceptionally bad hands. Thus the shuffling of fibers increases the uniformity of the yarn, but does not prevent groups of very good or very bad fibers from getting together and thus creating irregularities in the yarn.

Let us look inside one of our smaller mills. This mill has about 30,000 spindles on which yarn is spun. Prior to this spinning operation the fibers are shuffled and arranged end to end by a series of machines and are drawn down in

progressively smaller and smaller numbers to the proper number for spinning. Subsequent to the spinning operation there are found as many as six or seven hundred looms which weave the thread into cloth.

The mill we are discussing can process about 60,000 pounds of cotton each week. Were all this raw material being made into 30s yarn exclusively it would produce in a single working day about 170,000 miles of yarn, or enough to go nearly seven times around the earth's equator. To do this, approximately three million pounds of machinery are involved, requiring power at the rate of about 1250 kilowatts. In other words, this small mill processes about eight million million cotton fibers each week, or approximately thirty million fibers each second. To do this requires about 1/10 pound of machinery for each fiber delivered per second, or a ratio of fourteen million pounds of machinery for every pound of cotton processed per second.

From the above figures it may be seen that about 400,000 ergs of energy are required to carry each cotton fiber through the mill to its final resting place in a piece of cloth. Of these 400,000 ergs, the number required to impart the necessary twist per fiber to form the yarn is of the order of five ergs.[6]

A portion of the balance of the energy is certainly used in drafting the fibers and in imparting kinetic energy to the packages on which the cotton is wound temporarily. Undoubtedly a large proportion of the energy is consumed by the friction of the quarter of a million bearings in the machinery. This serves to illustrate vividly, not only the minuteness of the physical forces involved, but also the desirability of careful statistical control of the machines.

In this small mill about 200,000 pounds of cotton are distributed along the production line in the form of partial products. Of this only about 250 pounds, or slightly more than one-tenth percent, are actually being acted upon at any one time by the machinery. The bulk of the cotton in the mill is temporarily stored in cans or on bobbins, spools, and rolls for convenience in handling. This mass of cotton moves rather slowly through the mill, requiring about fifteen days to pass from raw cotton to cloth. It is from this parent body of cotton in its various forms that samples must be taken and measurements made.

The passage of fibers through a mill might be compared with the migration of electrons in an electrical circuit. The cotton fibers correspond to the electrons which are moving slowly but in large numbers through the conductor. A very interesting comparison may be formed between measurements made on yarn and those on the current in an electrical circuit. In electrolytic deposition of silver 0.00111800 grams of the metal are deposited in one second, when a current of one ampere is flowing. This corresponds roughly to 10^{18} ions per second, each carrying the charge of one electron. It is purely a coincidence, of course, that this number corresponds approximately, as we have seen, to the number of cotton fibers grown in the United States in one year.

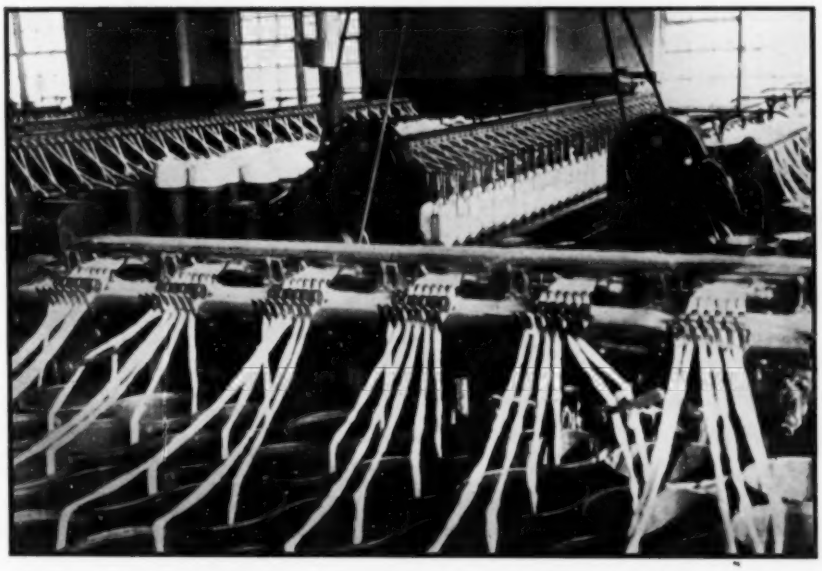

FIG. 2. "Shuffling" of cotton fibers in a mill by "doubling" and "drafting" slivers prior to spinning.

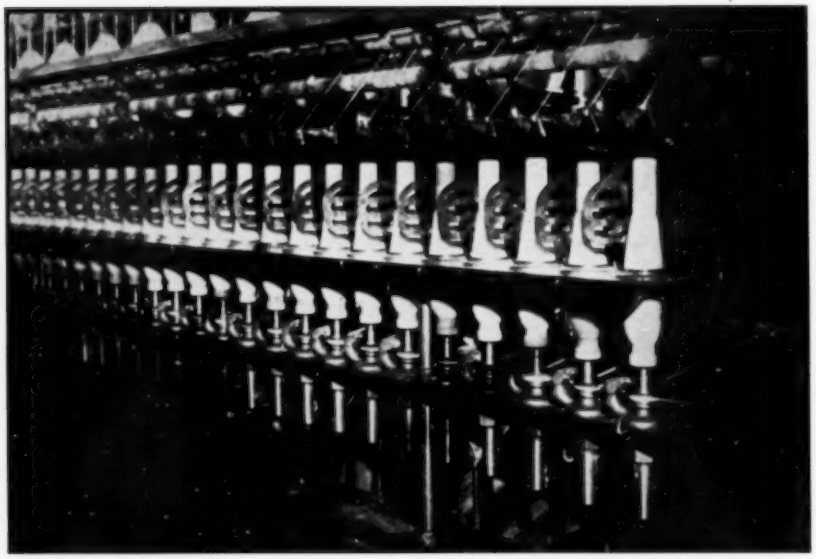

FIG. 3. The yarn is spun on bobbins which rotate at about 10,000 revolutions per minute. This picture shows a few of the many thousands of such bobbins in a mill. Note the "balloon" formed by the rapidly spinning yarn.

If we may think of the cotton fibers being processed at a given rate somewhat as electrons moving through a conductor and thereby giving rise to an electrical current, it follows that the entire United States cotton crop would have to be processed in one second to produce a "current" equivalent to one ampere.

We have seen that a small cotton mill having 30,000 spindles can deliver about 30,000,000 fibers per second to the cloth room in the form of finished goods. Were these 30,000,000 cotton fibers per second thought of as electrons per second, this rate of production would correspond to only about twenty micro-micro-amperes. It would require about 2500 years to collect and measure the properties of all the cotton fibers processed in this small mill to determine an average with the constancy that the current of one ampere can be measured by the electrolytic deposition method.

A single observation of the strength of yarn, for example, entails the rupture or separation of not more than about 100 fibers in the cross section of a 30s yarn. Thus, if predominately strong or weak fibers purely by chance happen to be together in the yarn, this measurement may be likened to the observation of a minute electrical current arising from a fluctuation in the velocity of not more than 100 electrons.

Electrical instruments which detect and measure such minute fluctuations and currents are of the most refined and sensitive types. Measurements on textiles may be seen therefore to be similar to those which might be made with an exceedingly sensitive instrument on a circuit which is not only greatly magnified but one in which a very minute current exists. A large number of observations must, therefore, be made on small groups of cotton fibers in order to estimate the probable value of the true average.

The present lack of basic measurements in the textile industry may be illustrated by the following examples. At a recent meeting of the Southern Textile Association,[7] a question addressed to prominent mill men was, "How do you find the new crop of cotton in comparison with the crop of other years?" From several opinions given, the most widely divergent were (1) that the cotton appeared better in every respect, and (2) that the cotton was not as good as that of previous years. No definitions of the vaguely qualitative terms *better* and *good* were given.

From this and many other similar instances it is evident that apparently even the same cotton behaves very differently under varying manufacturing conditions. It may be that the statements were justified on the basis of the particular observations that were made. But were these observations correctly made? Were the proper machine adjustments made to compensate for the characteristics of the new population of cotton fibers? Certainly neither condemnation nor praise forms any scientific approach to the problem of dealing with the annual Jonah of correct machine adjustments for new cotton.

Disconcerting conflicts of judgment frequently arise between conscientious men whose opinions are based unwittingly upon insufficient data which, in many cases, have been obtained through entirely different methods of measure-

ment and poorly controlled experiment. The essential point here is that there is no common basis for judgment. That is, from a research point of view there exists at present little controlled experiment from which conclusions may be drawn.

Other questions may be asked. How does the quality of yarn vary from the start to the end on a single bobbin? What is the average breaking strength or count of the yarn being produced in a mill today? What is the uniformity of the yarn? How does this uniformity effect weaving? At present to many such questions one may obtain a different answer from almost every person asked. Can there be no conciliation of these results? Indeed there can be, but it can be obtained only as a result of a thorough statistical appraisal of the many variables and conditions which exist in the cotton mill.

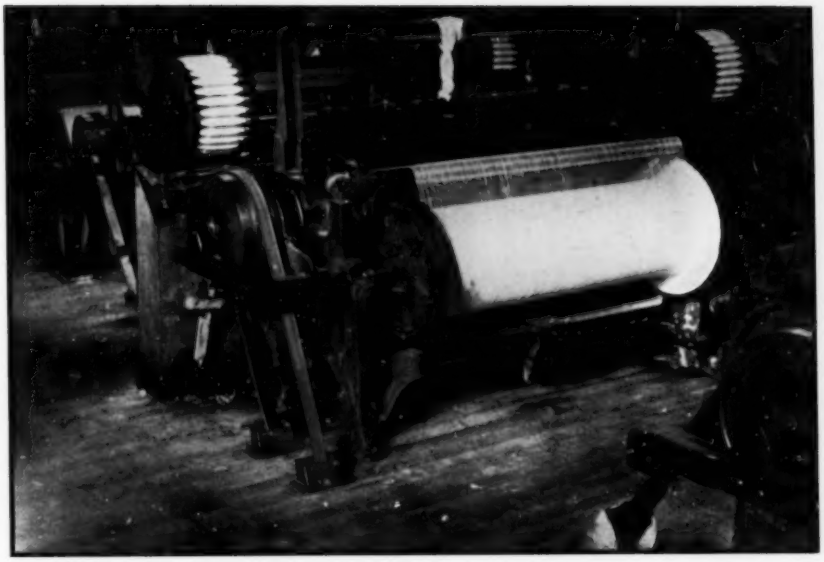

FIG. 4. A simple type loom for weaving the yarn into cloth. The warp threads are wound into the large "warp beam" in the foreground. The bobbins carrying the filling yarn may be seen in the automatic loading magazine at the upper left.

To restate more briefly, the need for statistical methods in the cotton textile industry arises from the great variability of the physical properties of the material and the large number of machines required to process the cotton. At present there is little or no control over the variables, not alone because of the difficulty of control, but also because of lack of sufficient knowledge. Such a complex situation can be understood and controlled only by resorting to methods of probability.

It is only through the coordination of events with cause that the benefits of knowledge may be derived. Thus, the solution of the problems in the textile industry are matters of logical interpretation rather than of statistical technique.[8] In this connection, it is essential that the statistician have a thorough knowledge of the underlying physical laws, as well as the practical nature of the problem with which he is dealing. Particularly during the early stages of the application of statistics in the field of textiles can the work be handled most effectively by well qualified statistician-physicists or statistician-engineers. There is danger that zealous statisticians, unfettered by an understanding of the physical realities and with the analytical tool at their command, may extract results which are not justified by actual conditions.

It is only of very recent date that schools have introduced special training in this *application of statistics* in the control of manufactured products, although courses in *pure statistics* have long been offered in departments of economics and mathematics. The methods of application of statistics to the control of industrial processes are ably treated by Shewhart,[9] Fry,[10] Deming, Birge,[11] and others.

The use of statistical theories in the solution of textile problems has several objectives. In the research laboratory statistical methods embody the principles for the analysis and interpretation of data so that justifiable conclusions and comparisons may be made. The related principles of mathematics provide the means for advances on the theoretical frontier of problems concerning the physical properties of the cotton fibers and their action upon one another and the behavior of the textile machinery. In the application to the manufacture of textile materials a statistical control of quality not only protects the customer, but also effects economies in the manufacturing process.

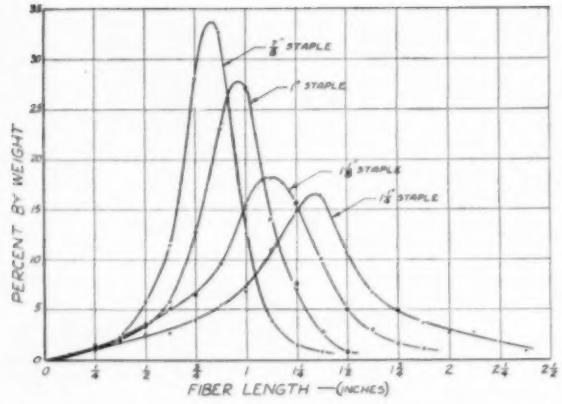

FIG. 5. Distribution of fiber lengths in four types of cotton populations.

In discussing the economic aspects of the application of statistical methods to industry, Shewhart[12] considers five general objectives. From one of these alone, *viz.* the determination of the minimum amount of inspection sufficient to give economic control of quality, he estimates that the Bell Telephone System saves annually more than enough to justify all of the attention that has been given to such studies. When it is recalled that the cooperative efforts of several hundred men over a period of five or six years were required to establish statistical methods in the Bell System, the economic significance of statistical methods may be appreciated.

Although the application of statistical methods to the textile industry requires time and patience before the full benefits may be attained, some results of practical significance and importance have already been obtained. In regard to the problems alluded to earlier in this paper, consider that of the quality of the yarn on a single bobbin. That the quality from start to end of the three miles of yarn on a single bobbin changes is a well recognized fact. Statistical methods, however, not only permit the correlation of this change with other phenomena, but also provide a significant comparison of the magnitude of this change in quality with those arising from other causes. Considerations such as these are extremely essential in establishing the proper methods of sampling.

If the spinnability of the cotton can be determined at an early stage in the processing, the cotton may be diverted to the manufacture of products for which it is most suited. If the quality of the product in intermediate stages of manufacture can be determined, proper machine adjustments for subsequent operations can be established.

Since it is unfeasible to reject defective material after the cotton has once started on its journey through the mill, it is desirable, as far as possible, to avoid the purchase of defective cotton. In the mill, a control of the processes must be maintained so that not more than a known amount of cotton becomes defective during manufacture. If these functions of statistical control operate properly it may become possible to practically eliminate the present practice of inspecting every yard of cloth produced in order to detect and remove defective material.

FIG. 6. A strand of cotton roving unwinding from a bobbin.

If we overlook the fibrous structure of a cotton yarn, the yarn and cloth may be considered to be continuous. Since the abnormal portions of either the yarn or the cloth are the result of both the random action of the machines and the variability of the physical properties in the cotton fiber populations, these abnormalities, or defects,

themselves occur at random in the yarn and cloth.

Statistical methods provide the means of determining the frequency with which any defect of specified magnitude and extent may occur in a given length of yarn or cloth. A contribution of exceptional practical value to the textile industry may possibly be made through the establishment

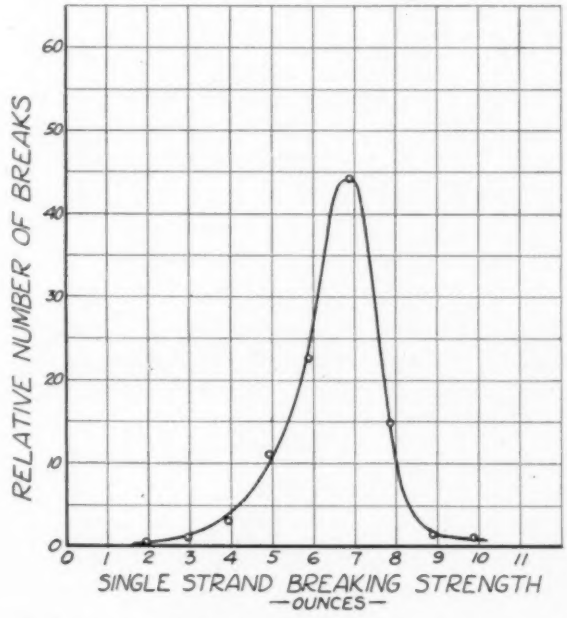

FIG. 7. A typical distribution of yarn breaking strengths.

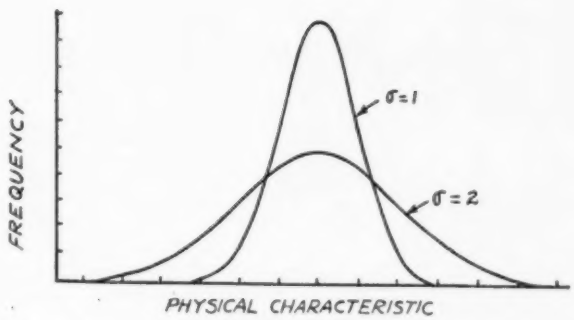

FIG. 8. Normal Gaussian curves. The observed characteristics of yarn present distributions similar to these.

of standards of quality which take these probabilities into account.

Thus, in conclusion, it should be evident that the solution of problems in the textile industry can be attained only through the application of all phases of statistical methods. By this is meant, not merely the statistical handling of data, but the complete study of sampling, instrumentation, techniques of measurement, probability theory, and statistical control of manufacture. In this way alone can significant data be obtained and reliable conclusions drawn. When such studies find themselves full-fledged and in common use, the manufacture of cotton textiles may be elevated from the state of an art to that of a science.

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Modern Theory of Solids. III

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This article, the last of the series, deals with the properties of the solid surface, and with the influence of impurities and flaws on certain volume characteristics. There has been very little theoretical work in these fields on the basis of the modern views. Consequently, a considerable part of what we shall say will be more or less speculative. We present these ideas in the hope that they may be suggestive, and caution the reader against embracing them uncritically.

VI. The Crystal Surface

(1) *The Surface Barrier: Thermionic Emission*

AT the surface of a crystal the potential energy of an electron rises and becomes asymptotic to the value zero (arbitrarily chosen) corresponding to infinite separation. The shape of the potential barrier at large distances is determined by the ordinary mirror image force. On the Sommerfeld picture, the valence electrons in a metal, at 0°K, fill a set of energy levels extending from the bottom of the inner "potential floor" to a height given by the Fermi-Dirac distribution function. The energy gap between this height and the height of the barrier is the work function, W. At higher temperatures, a few of the electrons will occupy states above the barrier, and some of these will be moving in the right direction to escape from the metal. An accelerating field at the surface effectively lowers the barrier and allows more electrons to escape. These simple ideas are illustrated in Fig. 29a.

The theory predicts that the electron current density from a metal at T°K, in the absence of an external electric field, should be

$$i = AT^2\epsilon^{-W/kT}.$$

The coefficient A should be a universal constant, $4\pi emk^2/h^3$, numerically equal to 120.4 amp. cm^{-2} deg^{-2}. The experiments,[1] on a wide variety of surfaces, check the exponential dependence on temperature and give a value of the work function W in good agreement with that obtained by other methods, such as photoelectric studies. In the constant A, only an order-of-magnitude agreement is found with the theoretical value. The experimental values vary from metal to metal, and among different samples of the same metal. The discrepancy is usually attributed to three factors: tiny surface irregularities, which make the actual emitting area larger than it appears to be; a possible slight dependence of the work function on temperature; and a "reflection," at the surface, of electrons which are energetically able to escape. Recent experiments on the distribution-in-energy of the emitted electrons[2] also seem to require a considerable reflection of electrons which have enough energy to escape. In discussing such reflection, the wave picture of electronic motion must be used, for a classical particle-electron moving toward the surface with energy in excess of the work function would be sure to escape. It turns out that the probability of reflection of a wave electron depends on its energy, and also on the shape of the surface barrier. It is greater, for example, for an abrupt, square-edge barrier than for a rounded-off barrier of the mirror image type. Thus far, attempts to invent a plausible barrier-shape which will give the required degree of reflection have not been particularly fruitful. The whole analysis is complicated by the fact that the experimental samples are polycrystalline wires, and there is unmistakable evidence that the work function is different for the different crystallite surfaces.[3] Difficulties of the same kind arise, of course, in the interpretation of photoelectric data. It seems evident that these points can be cleared up only

by a much more detailed picture of a metal surface than is available now.

With very high accelerating fields, an electron emission from cold metals can be observed, which increases with field strength according to the same sort of exponential law that governs the variation of thermionic current with temperature. The wave picture offers an explanation of this phenomenon of field emission. As the applied field is made very large, the surface barrier, in addition to becoming lower, also becomes fairly narrow near its top. Then a considerable number of electrons which have energies slightly less than that required for passing over the top of this narrowed potential hill, can penetrate through it and reach an external collector (Fig. 29b). Such penetration would, of course, be impossible for a classical particle-electron. The computation leads to an equation for the current which fits the observations fairly well, considering the difficulties of the experiments. It is to be noted that this penetration effect is supplementary to the reflection effect mentioned above. A potential barrier would separate a group of particle-electrons incident upon it into two sharp classes: those with energy greater than the barrier height would be totally transmitted, those with energy less than this height would be totally reflected. Wave electrons, on the other hand, are not so sharply segregated by a barrier, and the distribution-in-energy of the electrons beyond the barrier depends on its shape and thickness as well as on its height.

If we consider the wave nature of the electron within the solid as well as at the surface, and take account of the periodic field of the lattice, we arrive at the zone picture. Fig. 30 depicts the extension of the zones to the surface of a metal. The electronic charge distribution is also shown, decreasing exponentially away from the surface. The levels in the energy spectrum are not nearly so regularly distributed as they were on the Sommerfeld theory. We might expect this irregularity, which is a consequence of the separation of states into zones, to make itself evident somehow in the distribution-in-energy of electrons thermionically emitted. However, it can be shown that to a first approximation the variation of density of states is just compensated by the variation of velocity with energy within a zone (see V, 7). Except in special cases, the zone theory and the Sommerfeld theory predict the same results for thermionic experiments.

What can be said about the magnitude of the work function? Wigner and Bardeen[4] have shown that it can be divided into two terms. One of these arises from the attraction of the lattice ions for the electron, is completely independent of the nature of the surface, and is roughly proportional to the binding energy. The second term depends on the nature of the surface, and particularly on the dipole moment per unit area. The center of gravity of the electronic distribution associated with the last layer of ions may be displaced either to the right or left of the ion layer (Fig. 31). An electron in going through such a double

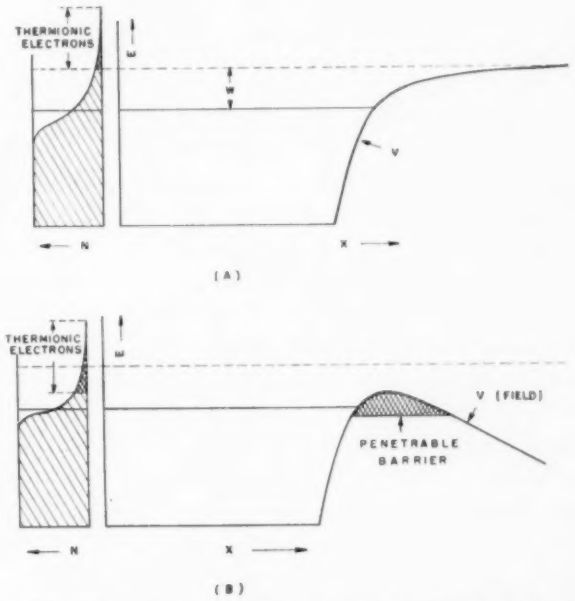

FIG. 29. Thermionic emission in the Sommerfeld theory. (A) Right: the course of the potential energy at the surface, in the absence of an applied field. Left: the Fermi-Dirac distribution in energy, at a temperature above 0°K. (B) An accelerating field lowers the height of the surface barrier and thus increases the thermionic current (Schottky effect). If the field is very strong, the barrier becomes so narrow that many electrons (on the wave picture) can penetrate through it.

layer of charge changes its potential energy by $4\pi eP$, where P is the moment per unit area. Bardeen's computations for a surface of Na indicate that the moment is quite small, and the same is probably true for pure metals generally. Table V, showing that work functions can be ordered with heats of sublimation, is

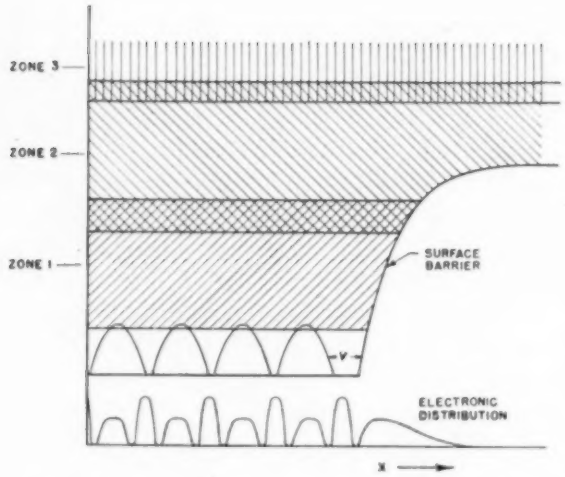

FIG. 30. Above: Extension of the zone type of energy spectrum to the surface of a metal. Below: distribution of electronic charge near the surface.

experimental evidence that the volume term in the work function is the predominant one. The direct experiments, also, show that the variation of work function among different crystal faces of the same metal is only of the order of tenths of an electron volt.

If a layer of foreign atoms is added to a metal surface, the principal effect on the work function is a change in the dipole moment. Thus, when cesium atoms are placed on tungsten they become ionized, losing their valence electrons, and the surface acquires a large positive dipole moment and a lowered work function. Conversely, when a cesium surface is oxidized, the oxygen atoms become negatively charged and the work function increases. We shall examine such adsorption processes later in more detail.

(2) *Surface Absorption of Light*

The stringent selection rules for volume absorption of light (see V, 5) do not apply to electrons at the surface of the crystal. An electron in the exponential tail of the charge distribution (Fig. 31) may make any transition which leaves unchanged the two components of its wave number vector σ lying in the surface. The component normal to the surface may change. Crudely, it is legitimate to regard the surface as a third body in the photon-electron collision, which can share in the conservation of momentum. The range of possible transitions, in metals and in insulators, is thus greatly broadened. Transitions to higher levels in the same zone are allowed, if these upper levels are unfilled.

This difference between the selection rules for surface and for volume absorption is particularly important in analyzing photoelectric behavior. For example, if all three components of σ had to be unaltered, in surface absorption, the low frequency limit of photoelectric emission would not generally correspond to the thermionic work function. If the electrons excited by surface absorption have enough energy to escape from the metal, they can be observed as an external photoelectric current. In the spectral photoelectric sensitivity curves this surface component usually passes through a maximum, corresponding to the maximum of the surface absorption (see Fig. 27) and is followed at shorter wavelengths by a component due to volume absorption.

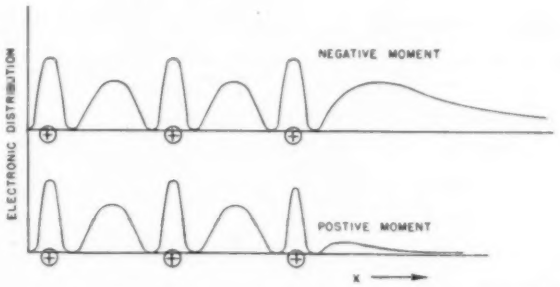

FIG. 31. Illustrates how the sign of the surface dipole moment depends on the distribution of electronic charge beyond the last layer of ions.

Adsorbed surface atoms, in addition to changing the work function, will greatly affect the electronic charge distribution near the surface and thus will affect its optical absorption behavior. An efficient photoelectric surface is one which combines low work function with high probability of surface optical absorption. In the commercial photoelectric surfaces, cesium on

TABLE V.

METAL	WORK FUNCTION	HEAT OF SUBLIMATION
K	2.24 ev	0.94 ev per atom
Na	2.25	1.13
Li	2.28	1.65
Ag	4.08	2.92
Mo	4.41	6.75
W	4.52	9.13

silver oxide on silver, apparently just these conditions are satisfied. The layer of cesium ions on the outermost surface provides a large positive dipole moment and therefore a low work function, while the layer of oxide between surface and metal is a region where there are many electrons which are not restricted by the volume selection rules.

(3) *Contact Equilibrium*

The behavior at contacts can be discussed with the use of the simple principle that, in equilibrium, the flow of electron across the boundary in one direction must be identical, in magnitude and in velocity distribution, with the return flow. When two different metal surfaces A and B are brought together, before contact the uppermost electrons in A, which has the lower work function, will lie above the uppermost electrons in B by just the difference between the work functions (Fig. 32a). After contact is made, electrons will flow from A to B, raising the potential of the interior of B, until the energy of the uppermost levels is the same in both metals. Even if the contact is not good, so that a potential hill exists between the two (Fig. 32b), electrons thermally excited over this hill will eventually establish this same equilibrium state, in which the net flow is zero.

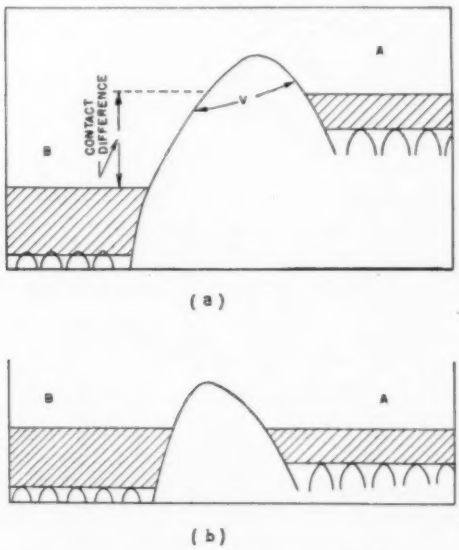

FIG. 32. (a) The contact potential difference between two separated metal surfaces is the difference between their work functions. (b) In equilibrium after contact is made, the tops of the filled bands in the two metals are at the same level.

The equilibrium arrangement requires special consideration when one of the solids is a semiconductor, as Wilson[5] has pointed out. The energy point in the semiconductor which corresponds to the upper edge of the filled band in the metal is not the upper edge of the highest filled band in the semiconductor, as one might at first suppose, but is about midway in the forbidden range between this filled band and the lowest unfilled band (Fig. 33). This is because the only electrons which can cross the boundary are those which, in one solid, occupy energy states which in the other are allowed, but unfilled. The electrons in both solids obey the Fermi-Dirac statistics. In both, there is an energy point about which, at $T>0°K$, the thermally excited electrons and the thermally vacated "holes" are symmetrically distributed. In the metal, this point is the top of the distribution at $T=0°K$; in the semiconductor, it obviously lies about midway in the forbidden region. And in equilibrium these points must coincide if the net flow is to be zero.

The same considerations apply to contact between a metal and an insulator, of course, since the difference between insulators and semiconductors is one of degree. It may be noted that the time required for equilibrium to establish itself, after contact, is limited by the rate at which electrons are thermally excited across the forbidden energy region in the nonconductor. When this gap is large and the temperature not high, the trend toward equilibrium may be very slow.

(4) *Contact Rectifiers*

Contact rectifiers generally consist of a semiconductor sandwiched between two pieces of metal. In the galena crystal detector of radio antiquity the crystal holder and the "catwhisker" were the two metals. In copper oxide rectifiers, the copper oxide is the semiconductor, the mother copper is one contact metal, and the arbitrary metal placed on top of the oxide is the other. This system has been rather fully investigated,[6] and we shall discuss it almost exclusively. Since the rectifier works satisfactorily when the upper contact metal is also copper, it appears that the

effect is fundamentally connected with a difference between the contacts of the oxide with the two metal surfaces.

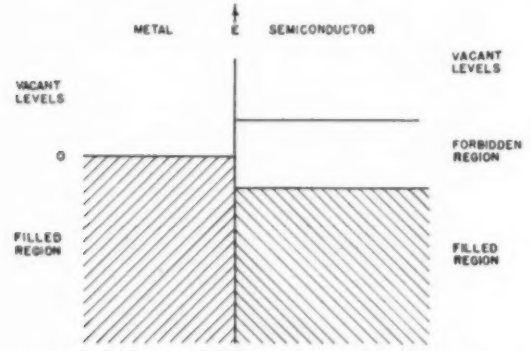

FIG. 33. Relative position of energy levels in a metal and a semiconductor at equilibrium. The top of the filled levels in the metal comes midway between the filled and unfilled bands in the semiconductor.

The first interpretation of the rectifying action is that offered by Schottky and his collaborators. They assume that most of the oxide layer contains excess oxygen, and on that account has a fairly low resistivity, but that a thin "blocking layer" of pure Cu_2O, with relatively high resistivity, occurs at the boundary between oxide and mother copper (Fig. 34). This picture is consistent with what is known about the mechanics of the oxidation process. The second contact, between the oxide and the second metal, is assumed to have low resistance. When a voltage difference is applied to the system, most of the drop is localized at the blocking layer, and an appreciable field emission (VI, 1) occurs across this layer. This field emission must be asymmetrical, of course, to explain the observed rectifying action: electrons must flow from copper to oxygen-contaminated cuprous oxide more readily than in the opposite direction. If the shape of the potential barrier were asymmetrical, such asymmetrical flow would result, but there is difficulty, as Schottky recognized, in inventing a plausible barrier shape which will account for the magnitude of the action. de Boer and van Geel have suggested that if one of the emitting surfaces is much rougher than the other, the concentration of the field at prominences will give the desired rectifying effect.

Wilson has proposed a later theory based essentially on the ideas of equilibrium between a metal and a semiconductor which we have outlined above. At equilibrium, the energy levels have the positions shown in Fig. 33, and the net flow of electrons across the boundary is zero. We must assume, in this theory of rectification, that the flow of current in either direction is practically zero for the energy levels below the forbidden region of the semiconductor. This property is very satisfactorily explained by the viewpoint of Gudden and Wilson, namely, that the region marked filled, in semiconductor of Fig. 33, contains bound electrons and holes which cannot move and, as a result, cannot conduct a current, even when there are holes present. We shall discuss this in VII. Suppose the metal is now placed at a higher negative potential (Fig. 35a). All the excited electrons in the energy range A are now available to flow into the semiconductor, so there will be a resultant flow in that direction. If the potential is reversed (Fig. 35b), the number that may flow from the semiconductor to the metal is unchanged, but the number that may flow from metal to semiconductor is decreased by those in the energy-range B. There are many more excited electrons in A than in B, since $OA < OB$. The result is an asymmetrical current voltage distribution of the type shown in Fig. 36, which is reproduced from Wilson's article. This theory assumes that the contact between the two solids is so good that an appreciable current may flow, and yet so poor that an appreciable voltage difference is maintained across the boundary. The Schottky blocking layer would furnish just this sort of contact. The curves of Fig. 36 were derived on the assumption of a barrier 10^{-7} cm wide, with square corners at equilibrium; the penetration through such a barrier, distorted by the field, was computed. In this special case the field emission tends to neutralize the rectification.

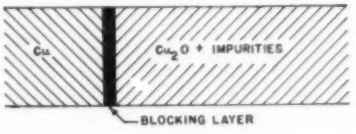

FIG. 34. Blocking-layer concept of the copper-cuprous oxide rectifier. The thin ($\sim 10^{-7}$ cm) layer of pure Cu_2O is a high resistance film. In Schottky's theory, rectification is due to asymmetrical field emission through this layer. Wilson's theory uses only its ability to withstand a potential difference between the copper and the contaminated Cu_2O.

(5) *Adsorption on Crystal Surfaces*

If an additional atom of the same material is brought up to a clean surface of a pure monatomic crystal, the energy states of the atom will broaden into bands which become identical with those of the crystal, and the additional atom will finally take its place as part of the lattice. The energy levels of the original crystal will also be affected, of course, but the effect per electron will be small, and the final crystal will contain just one more energy state in each zone.

Suppose, instead, that an atom such as Cs, having a low ionization potential (3.85 ev) is brought to the surface of a substance such as W, with a high work function (4.5 ev). We may expect the atomic states of the Cs atom to broaden out into bands in some fashion or other, depending on the structure of the W energy spectrum (Fig. 37). In the final energy spectrum of the entire system, solid plus adsorbed atom, the states in which a valence electron is about as likely to be found near the Cs atom core as near one of the W lattice ions, lie well above the states which are normally filled. This follows from the fact that the potential energy of an electron near a W ion is lower than it is near the Cs ion: the amplitude of the wave function, which determines the charge distribution, is therefore larger near the W ions, and this difference becomes unimportant only when the total energy is relatively large. The unequal charge distribution about Li and F cores in the LiF lattice (Fig. 20b) will be recalled as an example of this same effect. At equilibrium, then, the valence electron of the Cs atom will occupy one of the lower states, and the valence charge distribution about the Cs ion will be small. That is, the Cs will be effectively ionized, and will contribute as a positive ion to the dipole moment of the surface. The slight electronic charge about the ion will hold it to the surface, unless it acquires enough thermal energy to escape. We note that since this charge is present, the atom is not "entirely ionized."

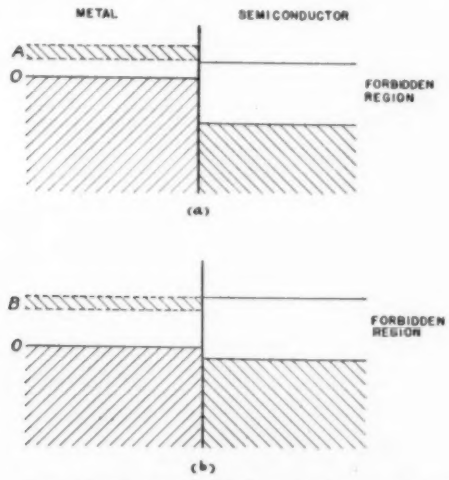

FIG. 35. Illustrating Wilson's theory of contact rectification. In (a) the metal is at a higher (negative) potential than at equilibrium (see Fig. 33), and the thermally excited electrons in A may flow into the semiconductor. In (b) the potential is reversed, and the electrons in B, which at equilibrium could flow into the semiconductor, can now no longer flow. Since $OA < OB$, there are more electrons in A than in B, and a rectifying action occurs. It is assumed that there is no flow below O.

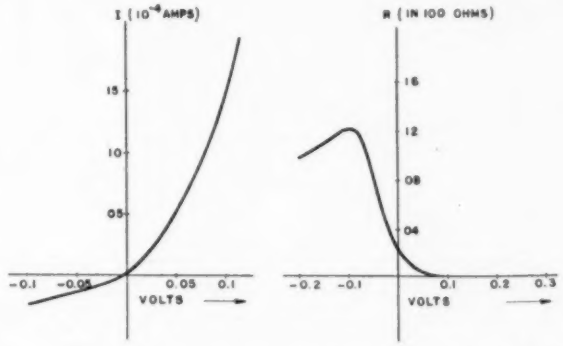

FIG. 36. Oxide rectifier characteristics predicted on Wilson's theory, assuming a blocking layer 10^{-7} cm thick. The scales are only typical.

Gurney[7] has emphasized that a certain degree of ionization of adsorbed atoms is to be expected, even when their ionization potential exceeds the work function of the metal. The relative charge distribution is determined by the relative potential fields around the lattice ions and around the core of the adsorbed atom, and these are better compared by comparing the ionization potentials of the two types of atoms, than by comparing the work function of the solid with the ionization potential of the adsorbed atom. Thus, Ca, Sr, and Ba all have ionization potentials greater than the work function of W but less than the ionization potential of W, and they are all partially ionized on W.

If the adsorbing crystal were some stable insulator, with the lowest band completely filled,

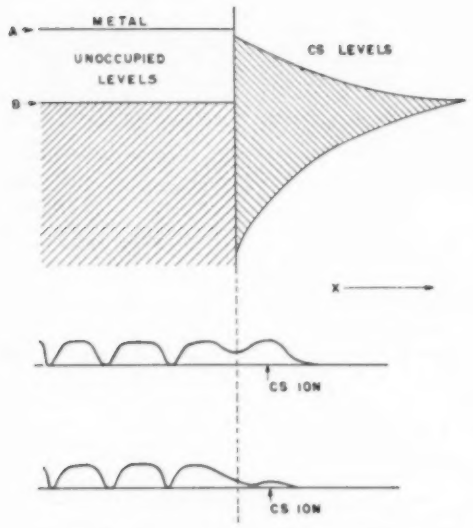

FIG. 37. Above: schematic diagram of the broadening of atomic Cs levels as a Cs atom approaches a W surface. Below: the upper charge distribution is that corresponding to an electron of energy *B* in the upper diagram; the lower distribution corresponds to an electron of energy *A* in the upper diagram. Since such low states as *A* are vacant in the metal, the Cs valence electron will occupy one of these, and the atom will be effectively ionized.

the valence electron of an adsorbed Cs atom would necessarily enter some higher state. This lowest possible level might easily occur in the forbidden region of the energy spectrum of the insulator (Fig. 38). The electronic charge distribution would be entirely localized about the Cs ion, and the level would be unbroadened, since there are no corresponding periodic states in the lattice.

Fig. 39 represents the hypothetical behavior of the energy levels when an atom of high ionization potential, such as O, is brought to the surface of a crystal of low work function, such as Cs. Two of the atomic levels of O are shown leading into the forbidden region of the Cs energy spectrum, *below* the band occupied by the Cs valence electrons; the levels are unbroadened, since there are no corresponding states in the lattice. At equilibrium, these discrete levels lying below the filled range in the Cs spectrum will be occupied by valence electrons from the Cs lattice, and these electrons will be entirely localized about the O atom. This redistribution of charge may be interpreted as the formation of a molecule of Cs_2O; however, since the entire lattice has contributed the two valence electrons, it is scarcely legitimate to think of two particular Cs atoms as involved in the "molecule." Another way of saying this is, that the mobility of an oxygen atom on a cesium surface is not directly connected with the heat of dissociation of Cs_2O.

In a case where the difference between ionization potential and work function is less extreme (O on W is perhaps an example) the atomic states might lead into the filled region of the spectrum of the solid. They would then become broadened, and any valence electron of the crystal would have a probability of being found near the core of the adsorbed atom. If the field of this core is strongly negative, compared with the field of a lattice ion, the wave functions will have a larger amplitude near the adsorbed ion than within the lattice; the atom will have, statistically, a negative charge, and the surface will have a negative dipole moment and an increased work function.

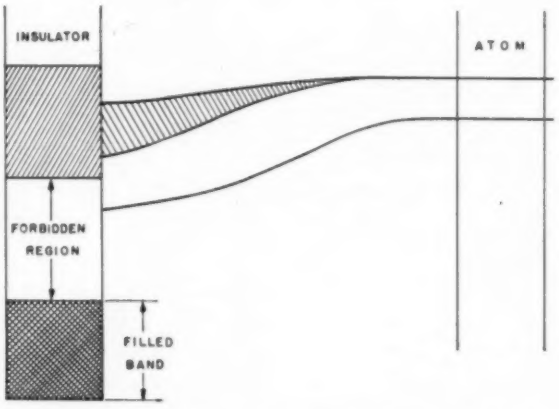

FIG. 38. Illustrates how some atomic levels are broadened while others remain narrow, when the atom is adsorbed on an insulating crystal.

It is interesting to return to the case of Cs atoms added to W, and see how the surface ultimately becomes one of Cs. As more and more Cs atoms are added and ionized, the tungsten obtains an increasing negative charge and the energy of its valence electrons becomes higher and higher, nearer to the energy of a valence electron in an isolated Cs atom. Eventually a surface concentration is reached at which additional Cs atoms are not appreciably ionized, and the electronic charge distribution extending beyond the W lattice becomes comparable with that around the Cs ions in metallic cesium. There

is experimental evidence that this stage is reached when the surface is about two-thirds covered. Thereafter, the lowest state for the Cs electron is one in which it is approximately as likely to be found near the Cs ion as near any W ion in the lattice. Moreover, the way in which the atomic levels spread begins to resemble the way they spread when additional Cs atoms are brought up to a Cs lattice, and eventually becomes identical with it, when the surface is covered with a layer or two of Cs. Thereafter the Cs atoms form a Cs crystal, and finally we have two bulk metals in intimate contact.

(6) *Surface Electron States*

One very important effect of bounding a crystal with a surface is the following: additional allowed energy states are brought into the energy spectrum. Electrons in these states are not free to travel through the lattice, but are bound at the surface. To see how these states arise, it is necessary to look a little more closely into the origin of the zone type of energy spectrum for an infinite lattice. When the Schrödinger equation (see III, 1) is solved for a periodic potential field, two types of solution are found. One of these types, valid for certain ranges of the total energy, is a periodic function, which leads to a periodic probability distribution and to a finite probability of finding the electron at any point in the lattice. The energy levels going with these solutions we have called the "allowed states," and the energy-ranges for which these solutions are valid are the "allowed regions" in the energy spectrum. The solutions of the second type are real exponential functions, rather than periodic functions. They lead to probability distributions which decrease exponentially in one direction and increase exponentially in the opposite direction. Such unbounded solutions do not correspond to any physical property of the electrons, so they are ruled out of consideration, and the ranges of total energy for which such solutions occur are the "forbidden regions" of the spectrum. Tamm[8] has pointed out that when the crystal is not infinite, but has a surface, it is no longer necessary to discard all these solutions of the second type. If we choose those which decrease exponentially inward from the surface, their exponential increase in the opposite direction, which would occur if the crystal were infinite, is halted at the surface. Outside the crystal, where the potential energy is greater than the total energy, the function is rapidly damped out. The result is a bounded probability distribution, physically reasonable, which corresponds to an electron localized at the surface, in an energy state between the allowed bands of periodic states (Fig. 40). The probability distribution is periodic in both directions on the surface; electrons in these states will be free to move about on the surface. It turns out that the number of these localized levels is approximately equal to the number of surface atoms. The volume properties

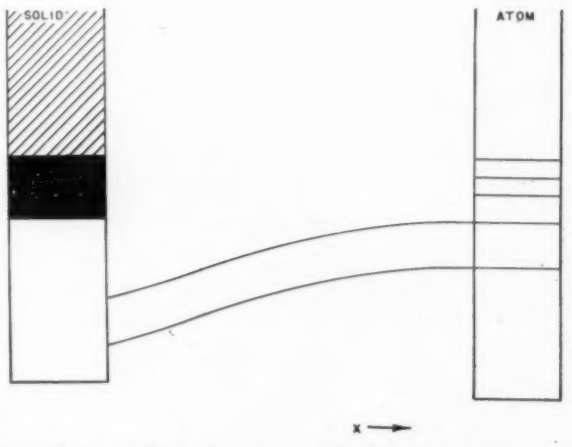

FIG. 39. Adsorption of an atom of high ionization potential on a crystal with low work function.

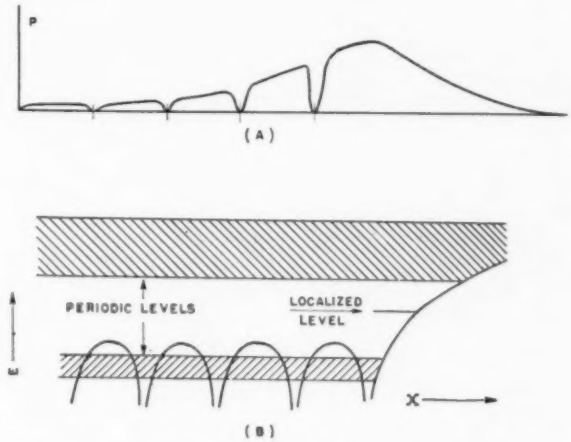

FIG. 40. (A) Charge distribution associated with a state in which the electron is localized at the crystal surface. (B) The localized surface state is represented by a line at the position of localization.

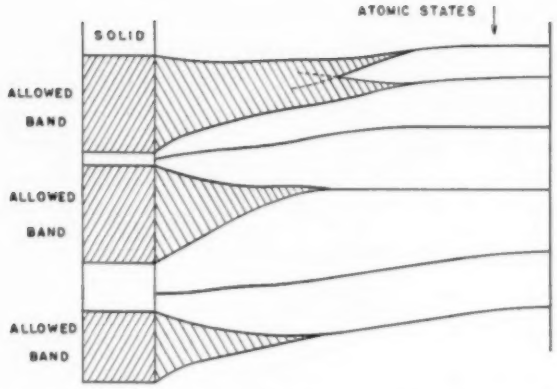

FIG. 41. Symbolizes the behavior of the atomic states of an impurity atom, when the atom is placed in the interior of a solid. Some of the levels are broadened; others become discrete levels in the "forbidden regions."

of a crystal of ordinary size, therefore, are not greatly affected by the presence of these states, even when all of them are occupied.

In metals, with overlapping zones of periodic states, these surface levels cannot be expected to influence even the surface behavior greatly, since an electron in one of them can easily make a transition to a nearby periodic state and be free to travel through the lattice. In an insulator, on the other hand, it is possible for an electron to become "trapped" in such a localized state between two allowed regions in the volume spectrum. It is to be noted that these states can occur, not only at the external surface, but also at cracks and crystal boundaries within the sample.

VII. Modification of Volume Properties by Impurities

(*1*) *Additional Energy States*

We have seen that in a perfectly regular lattice all the atoms cooperate to give an electronic spectrum which consists of allowed and forbidden energy ranges. Any impurity atom, whether it is a "replacement" or an "interstitial" impurity, will break the regularity of the lattice and will induce certain changes in the energy spectrum, just as a surface induces changes (VI, 6). We can get an idea of the sort of changes an impurity atom causes, if we visualize the operation of bringing an impurity atom into the lattice. Some of the energy levels of the atom will broaden out into bands which will join with the allowed bands of the solid; others will go into discrete states in the forbidden ranges (Fig. 41). The probability distribution going with a level in one of the allowed bands will be periodic at large distances from the impurity atom, just as if the irregularity were not there (Fig. 42a). The probability distribution for the discrete levels, contrastingly, must damp out exponentially in all directions from the impurity atom (Fig. 42b). An electron which happens to occupy one of these discrete levels is localized in the neighborhood of the impurity atom. If the impurity atom is one which has a dense spectrum of energy levels (Fe or Mn, for example) and the solid is a good insulator, with wide energy gaps between allowed bands, there may be several such localized levels about each impurity atom.

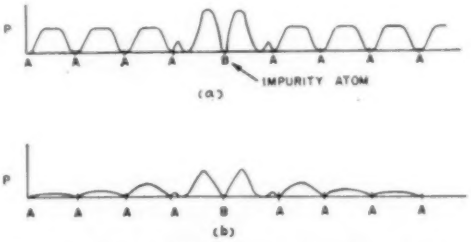

FIG. 42. Symbolizes the charge distribution about an impurity atom: (a) associated with one of the periodic states; (b) associated with a bound state in one of the forbidden regions. The impurity atom is *B*, the atoms of the pure crystal are *A*.

We shall examine several hypothetical cases to see what will be the effect of the additional states —both the periodic and the localized levels—on the electrical conductivity. Suppose, first, that an atom of an insulator is replaced by an impurity atom, which has a set of energy levels that go over, each one, into an allowed zone of the original energy spectrum. The number of levels in the new spectrum will then be the same as in the old. Suppose, further, that the impurity atom has fewer valence electrons than the atom it replaced. There will then be some "positive holes" (i.e., vacant levels) at the top of the previously filled band of the insulator, and the presence of these holes will lend the solid an electronic conductivity. This conductivity will increase linearly, at first, with concentration of such impurity atoms, and, like ordinary metallic

conductivity, will increase with decreasing temperature. When the impurity atoms become so numerous that they are in a "combining ratio" with the original atoms, a completely regular lattice may again form, with its own distinctive energy spectrum. Similarly, the presence of a discrete impurity level below a filled band of an insulator (Fig. 43a) will also give the crystal an electronic conductivity, if this level is not normally filled by an electron of the impurity atom. In equilibrium, this low level will be filled by an electron from the upper band, and the hole left in this upper band will be available for conduction.

If a localized impurity state lies between the filled and unfilled bands of an insulator, and is normally occupied by an electron of the impurity atom (Fig. 43b), this electron may be thermally excited into the upper unfilled band where it will be available for conduction. If the gap between localized state and upper band is small compared with the gap between bands, thermal excitation from the localized state will be very efficient, compared with thermal excitation from the lower band. Such a substance would act as a semiconductor with a smaller energy gap than is characteristic of the pure state. It is generally believed that in most semiconductors the observed low value of the energy gap (see Table II) is to be attributed to the presence of such impurity states. Gudden has shown that the energy gap as measured by the frequency threshold for photoconductivity, is usually much larger than the value which fits the data on variation of conductivity with temperature. Because of their sparsity, the impurity states could not be expected to absorb light appreciably; the threshold for photoconductivity should therefore give the true value of the gap between filled and unfilled bands in the pure substance. In cuprous oxide, for example, the E derived from plots of log conductivity *versus* $1/T$ is 0.6 ev, while the photoconductivity experiments give a value near 2 ev.

When the original pure substance is a metal, the additional states which are associated with an impurity atom will evidently not have any marked effect on the conductivity. The impurity atom will increase the resistance chiefly by interrupting the regularity of the normal lattice as a scattering system for the electronic waves. This effect of impurities in a metal is very noticeable at low temperatures, since it persists after the irregularities due to thermal lattice vibrations have largely disappeared (see V, 7).

(2) *Fluorescence and Phosphorescence in Crystals*[9]

The phenomena in this field can be crudely summarized as follows: a solid absorbs light of one wave-length, and sooner or later emits light of a different (longer) wave-length. If the time between absorption and emission is immeasurably short, the effect is called fluorescence; if there is a measurable lag, the effect is called phosphorescence. Both types of response may be present in the same material. The observed behavior is extremely varied, and nothing like a comprehensive theory, on any basis, has been worked out. The ideas presented here are intended to suggest how the general phenomena may be fitted into the zone picture.

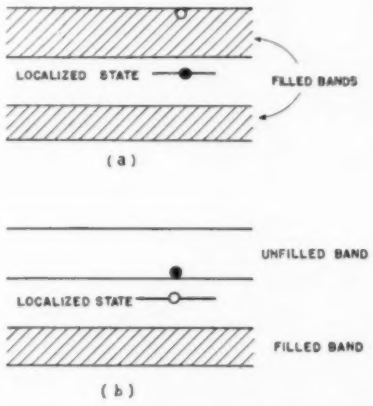

FIG. 43. In (a) a localized state due to an impurity atom lies between two filled bands of the solid, and is not filled by an electron of the impurity atom. It will be filled by an electron from the upper filled band, and the presence of the vacant state (positive hole) in the upper band will contribute to the electronic conductivity of the solid. In (b) the localized state lies between a filled and unfilled band of the solid, and is normally occupied by an electron of the impurity atom. This electron is more apt to be thermally excited to the upper band than is an electron in the lower filled band. Such impurity states may account for the high conductivity of many semiconductors.

Suppose the crystal is a pure insulator, with a wide energy gap between the highest filled band and the lowest unfilled band. When a quantum is absorbed, an electron will make a transition from some state in the filled band to the corresponding state in the unfilled band. Both this electron and the positive hole it leaves will be free to move throughout the lattice—en-

tirely independent of each other, if we neglect the possibility of a correlation between the two (see V, 6). Due to collisions with the lattice, both the electron and the hole will quickly lose whatever kinetic energy they have retained from the absorption, in excess of thermal energy. That is, the electron will fall to a level near the bottom of the upper band, and the hole will rise to a level near the top of the lower band (Fig. 44a). Assuming that the mean free path is 10^{-5} cm, and that a few percent of the excess kinetic energy is lost at each collision, the time for this thermal equilibrium to be established is about 10^{-9} sec. At low temperatures the mean free path will be longer, and the time to reach equilibrium will be proportionately longer. How long can the electron be expected to remain in the excited state? If we assume that electron and hole cannot "recombine" unless they come within a distance of 10^{-8} cm of each other, a simple computation shows that the mean lifetime is about 10^{9} sec., if there is only one excited electron in a crystal of volume 1 cm^3. This mean lifetime decreases with increasing concentration of excited electrons and holes, of course: if n_0 excited electrons per cm are present at time $t=0$, and the collision radius is assumed to be about 10^{-8} cm, the number present at time t is readily found to be

$$n(t)=\frac{n_0}{1+n_0 t/10^9}.$$

If the bands are narrow and the gap wide, the frequency of the quantum emitted when recombination takes place will be approximately the same as the frequency of the quantum originally absorbed—the fluorescence will be a resonance fluorescence.

When impurity atoms are present, furnishing localized levels between the allowed bands of the normal energy spectrum, either the excited electron or the hole, or both, may, in place of recombining directly, become trapped in these states. Such a case is depicted in Fig. 44b. Two impurity levels are shown. A valence electron of the impurity atom, which normally occupies the lower level, has neutralized a hole left in the lower band by optical excitation of an electron to the upper band. This excited electron, in turn, has fallen into an upper state, normally vacant, of another impurity atom. Obviously, the fluorescent quantum emitted in either of these trapping processes will have a longer wave-length than the original absorbed quantum. The probability of such trapping, as compared with the probability of direct recombination, will naturally depend on the concentration of the impurity atoms. Commercial willemite, for example, contains about 1 percent of Mn as an "activator" in a zinc silicate matrix. This is a density of about 10^{21} Mn atoms per cm^3; for this concentration, trapping, assuming a capture radius of 10^{8} cm, turns out to be very much more probable than direct recombination.

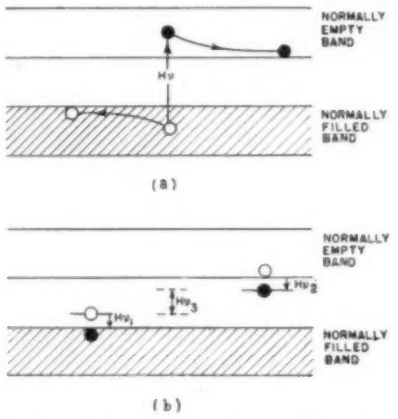

FIG. 44. (a) Shows schematically how an electron, after optical excitation, is separated from the lower vacant state, and how both the electron and this positive hole lose their excess kinetic energy to the lattice. (b) Shows the possibility of trapping an electron and a hole in localized states of impurity atoms, with emission of fluorescence quanta of frequency ν_1 and ν_2. The energy $h\nu_3$ is still available, to be used in a phosphorescence quantum of frequency ν_3.

After an electron and hole have been trapped, the lattice still contains energy represented by the gap between the upper localized state containing an electron and the lower localized state containing a hole (i.e., vacant). Two sorts of processes can be imagined which will result in the release of this energy as a quantum of phosphorescent light. The electron may be thermally excited from the bound state to the upper band, where it will be free to travel through the lattice, and will have a finite probability of encountering a hole and neutralizing it. Or the impurity atoms themselves may migrate in the crystal, through the lattice or along internal cracks. When one of these impurity atoms which contains an extra "trapped" electron meets another which contains a trapped

hole, neutralization and emission of a quantum of phosphorescent light may be expected. The rate at which either of these processes occurs will, of course, depend exponentially on the temperature. Actually, the rate of decay of phosphorescence is observed to become very low at low temperatures.

We have said that the phenomena in this field are extremely varied. It seems that the modern theory offers approximately the required degree of leeway for explaining them, but a much more complete picture of the energy spectra is necessary before any quantitative comparison with experiment can be made.

(3) *The Latent Photographic Image*

The formation of a latent image by absorption of light in the silver halide crystals of a photographic plate, is presumably a special aspect of the general field of crystal fluorescence and phosphorescence. Several writers have tried, with considerable success, to account qualitatively for the major photographic phenomena on the basis of the modern picture of electronic energy levels in the halide crystals.[10] Gurney has suggested that the formation of the latent image is a trapping, in localized states belonging to impurity atoms, of electrons which have been optically excited to a conduction band. These electrons need not have been originally in a filled band of the crystal, but may have been in localized levels above the filled band. It is quite plausible that the various methods of sensitizing plates to light of long wave-length are effective because they provide a large number of such levels not very far below the upper band, which are normally filled with electrons.

To account for certain of the observations, such as the development of the plate grain by grain, it seems necessary to add another complication: the localized levels, after trapping electrons, are supposed to congregate together, somehow, in clusters of ten or so which form the centers of the developable image. Such aggregates are presumed to be more stable than the isolated levels, though they may be broken up by light of a suitable frequency (Herschel effect). The collision of a bound electron with a hole, during the migration to form a developable center, will result in neutralization of the pair and in reversal of the effect of the original light absorption. The probability of this occurrence is proportional to the square of the number of pairs present. The formation of the latent image should therefore be less efficient at high light intensities than at low intensities—this is the proposed explanation for the breakdown of the reciprocity law (blackening proportional to intensity and time) at strong illumination. A breakdown of the reciprocity law is also observed at weak illumination: the efficiency of production of a latent image is low when the light intensity is very low. Webb has suggested that this may be due to a dissociation of the developable center, when it begins to form, by thermal excitation of the first few trapped electrons. The stability of a center is supposed to increase with the number of trapped electrons in the center. At low light intensities, the centers will grow very slowly, and small centers just starting will have a relatively large probability of thermal annihilation. The inefficiency at low light intensities becomes more serious as the temperature is raised, a fact which is consistent with Webb's hypothesis.

We remark again that the modern picture of the electronic structure of solids is only beginning to be applied to such effects as fluorescence and the latent image, and that most of the current "theory" is necessarily speculative in nature and subject to considerable modification. There is a great necessity for many experiments in these fields, guided by the modern viewpoint. The efficient fluorescent powders which are technically important, and the highly complicated modern photographic emulsions, are probably not the ideal experimental materials in the present crude state of our knowledge. Experiments with single crystals of the alkali halides, such as those which Pohl and his collaborators have been carrying on for a number of years,[11] seem to offer the most direct course to a clearer understanding of these phenomena.

VIII. Plasticity and Rupture of Crystals

During the past few years there has been much investigation of the mechanical properties of single crystals, and considerable progress has been made toward an atomistic picture of the

TABLE VI.

	Glide Plane	Glide Direction	Critical Shear
Cu	(111)	[10$\bar{1}$]	0.10 kg/mm²
Mg	(0001)	[11$\bar{2}$0]	0.083
Sn	(100)	[001]	0.189
	(110)	[001]	0.133

behavior of polycrystalline material. These subjects are, in the main, well beyond the scope of the zone theory in its present state of development. We shall present a very brief survey of some of the more elementary experiments and theoretical ideas.[12]

(1) *Shear Translation in Single Crystals*

Single crystal rods of all metals obey Hooke's law, under tension, up to a certain critical stretching force; beyond this point they undergo permanent inelastic deformation. The critical force depends on the history of the particular specimen and on its crystallographic orientation. Examination of a stretched rod shows that the deformation consists in a slipping of sections of the rod relative to one another, along certain lattice planes, and in certain directions in those planes. Usually the gliding occurs along only one family of low index lattice planes, though in some cases (e.g., tetragonal β Sn) two sets of glide planes appear. The gliding direction in the glide planes is also a fixed simple lattice direction.

The critical shearing stress (i.e., the component, in the gliding direction, of the stretching tension at which plastic deformation just begins) is a characteristic of the material. It may vary from specimen to specimen by a factor of about 5, depending on the purity and previous history of the sample. Characteristic values are listed in Table VI. The critical shearing stress decreases rather slowly with increasing temperature up to the neighborhood of the melting point. It is greatly increased by previous stretching—the material becomes "shear strengthened." An elongation of 100 percent may increase the critical stress by as much as 20 times; that is, the range of stress over which the material follows Hooke's law is greatly extended. Annealing of the stretched sample brings its critical shearing stress back to the original low value.

Ionic crystals, if they are first well annealed, show this same kind of glide deformation. Rocksalt, for example, glides along (110) planes in the [110] direction when a critical shearing stress of about 0.075 kg/mm² is exceeded. This is of the same order of magnitude as the value for metal crystals (Table VI). The extension possible before breaking occurs is generally much less than for metals. The same sort of shear strengthening is observed, and reannealing removes the shear strengthening. The critical shearing stress seems to vary more rapidly with temperature.

(2) *Breaking Strength of Single Crystals*

A single crystal which has been stretched to a certain point will break in one of several definite simple crystal planes. Breaking occurs when the tension normal to the breaking plane exceeds a critical value which, like the critical shearing stress, varies somewhat among different specimens, depending on their purity and history. The extent to which the crystal can be stretched before it breaks depends on the ratio of the critical stresses for gliding and for breaking; the crystal is plastic if the former is relatively small, and brittle if it is relatively large. The breaking plane need not be the same as a glide plane. Typical values of breaking stress are given in Table VII. The breaking stress, like the critical gliding stress, is slightly dependent on temperature, increasing at low temperatures. In NaCl the breaking stress, unlike the critical shearing stress, increases above room temperature; it is about 8 kg/mm² at 600°C.

TABLE VII.

	Breaking Plane	Critical Stress (kg/mm²)
Zn	(0001)	0.18
	(10$\bar{1}$0)	1.81
Bi	(111)	0.29
	(11$\bar{1}$)	0.69
Fe	(100)	0.30
NaCl	(100)	0.22
CaF_2	(111)	1.55

(3) *Theoretical Values of Critical Stresses*

One of the first attempts to estimate the breaking strength of a perfect lattice was made by Polanyi.[13] From the surface tension of liquid

NaCl, he estimated the energy, α, necessary to form a unit area of surface of crystalline NaCl, and assumed that the work done in breaking the crystal is essentially the energy necessary to form the two new surfaces. If the mean distance of action of the forces between the two surfaces is l and the normal stress at breaking is S, the relation $2\alpha = Sl$ should be expected, roughly. Using Polanyi's value of α and the observed S, one finds $l = 1.4 \times 10^{-5}$ cm, which is implausibly large. Taking $l = 5 \times 10^{-8}$ cm as a reasonable value, one finds $S_{\text{ideal}} = 61$ kg/mm^2, which is about 300 times the observed value. Zwicky[14] carried through a more accurate calculation on the basis of the Madelung-Born theory and found $S_{\text{ideal}} = 200$ kg/mm^2 for NaCl. Similar calculations have been made for a number of other substances: a typical set of values is given in Table VIII.[15] Similar estimates of the critical shearing stress have been made by Frenkel, using the Madelung-Born model. Again, as with the breaking strength, the theoretical value turns out to be of the order of 1000 times the observed value.

While the Madelung-Born model is not suitable for precise calculations (see IV, 2) it should certainly yield a result closer to the actual value than a factor of 1000. For the explanation of the observed low critical stresses, we must look to some fundamental difference between the real crystals on which the experiments are made and the perfect crystal which the theory treats.

Griffith[16] has shown that tiny surface cracks, at which stresses accumulate, are a very likely cause of low strength. He computed the stress distribution in the neighborhood of a long cylindrical hole, with an elliptical cross section, in an isotropic elastic solid, and found that the stress at each end of the major axis is 1000 times the average stress, if the ellipse has a major axis 500 times its minor axis in length. Thin narrow surface cracks of this general shape are not at all implausible. It is easy to see that rupture, once started at such a fissure, will proceed "explosively." As the cross section diminishes while the load stays constant, the average stress increases, and the stress at the edge of the crack increases proportionately. Griffith found, experimentally, that thin rods of glass and quartz were very strong and pliable just after they were formed, but became quite brittle when the surface was scratched. Experiments by Joffé, on rocksalt, and by Orowan on mica, support this interpretation of low breaking strength.

TABLE VIII.

	PLANE	S (ideal)	S (obs.)	RATIO
αFe	(100)	1350 kg/mm^2	0.30	4500
Zn	(0001)	360	0.18	2000
	(10$\bar{1}$0)	1250	1.82	700
Bi	(111)	350	0.32	1000
NaCl	(100)	200	0.22	1000
CaF_2	(111)	900	~2.2	400
Mica	(001)	2300	~230	10
SiO_2	(11$\bar{2}$0)	1000	11.6	90
	(0001)	800	85	90

The low value of critical shearing stress, on the other hand, is apparently not connected, experimentally, with the presence of surface cracks. Taylor[17] has proposed that small thin cracks are distributed throughout the volume, and that the stresses are magnified at the edges of these. This idea, placed in a quantitative form, gives rather good agreement with the stress-strain observations. Strengthening by shear is supposed to be due to a decrease, during gliding, of the average length of the cracks, which would reduce the stress-magnification at their edges.

It will be noted that the thin cracks which, on Taylor's theory, are distributed throughout the volume of a well-annealed crystal, would divide the crystal into a number of tiny blocks. There is an abundance of evidence, from many other sorts of investigations, that a mosaic structure of this general type exists in most crystals, and there have been several suggestions as to its origin. Zwicky[18] at one time proposed that such a mosaic is thermodynamically more stable than the perfect lattice, but this view has not been generally favored.[19] The theory of "lineage structure" developed by Buerger,[20] which attributes the imperfection to irregularities inevitably included in a crystal as it grows, seems to be particularly plausible and promising.

It is a pleasure to acknowledge our deep indebtedness to Dr. Saul Dushman for his generous advice and criticism during the preparation of these articles.

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Science has a true international mission. Far from choosing propagandistic methods to promote internationalism, science creates the true atmosphere of humanity as a common bond of the many diversified races and nations, just as the universe of radiation is the super unit of light and heat, of death rays and life rays. As it is important to recognize the facts and advantages of racial and national differences, so it is equally important to consider nationalism only as a first step towards true international understanding, based upon respect and appreciation for the services of each individual nation to humanity.

E. WEBER—"The International Mission of Science,"
Scientific Monthly

Moisture in Textiles*

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New York, New York

MARCO POLO described cotton cloth which he saw in India as of such exquisite fineness that it was termed "webs of woven wind." This fine quality was due to the skill and patience of the workmen in the hand processes of spinning and weaving, rather than to any superiority of Indian cotton, since it is well known that Indian cotton is by no means the best in the world. It is said that an important factor contributing to the fineness of this cloth is that the moisture imbibed by the cotton fibers from the thumb and finger during the formation of the thread more perfectly incorporates the fibers into thread than can be done by the use of any mechanical means.

The question of moisture content, and therefore of atmospheric humidity, is important in all of the processes used in the manufacture of cotton cloth. The machinery and the cotton passing through it generate a certain amount of electricity which imparts a static charge to the fibers, causing them to separate or curl up, thus affecting the smoothness with which the work runs. Cotton manufacturing is therefore facilitated by a humid atmosphere which permits the static charges to leak off the fibers more readily and reduces the amount of electricity generated. Localities with an unusually moist climate formerly possessed a great advantage over districts less favored in this respect. Lancashire, England, and New Bedford, in this country, provide such a natural advantage, although this has been partially attained elsewhere by artificial humidification.

It seems appropriate therefore, in this symposium, to show how a study of the electrical properties of textiles and their dependence on atmospheric conditions and naturally occurring impurities in the material, not only has resulted in important economies and improvements in the use of textile insulation in the electrical industry, but also has contributed to the general knowledge of the properties of fibrous materials.

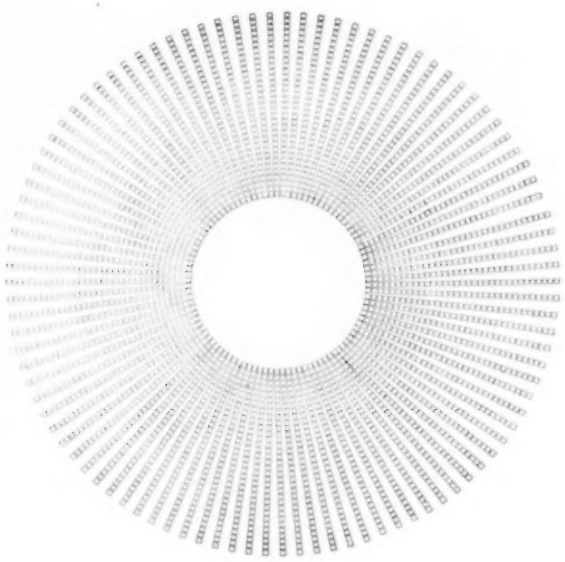
The electrical insulation resistance of textiles, when dry, is enormous compared with the resistance observed under atmospheric conditions. This difference has been rightly ascribed to paths of moisture within the structure of the material, along which electric current can flow. Also, it has long been known that silk is a better electrical insulating material than cotton. Since cotton absorbs materially less moisture than silk under equivalent atmospheric conditions, the electrical superiority of silk is somewhat surprising.

The immediate objective of work initiated at the Bell Telephone Laboratories some 12 years ago was to investigate the reason for this difference in the electrical behavior of cotton and silk. The important result of this work was the discovery that by washing electrical insulating cotton in water, the insulating value could be improved to such an extent that its adoption as a substitute for unwashed silk as textile insulation on telephone cords, wire and cable has resulted in annual manufacturing economies of several hundred thousand dollars.

This is an instance of what is common experience in research; some by-product of a systematic investigation may become much more valuable than the direct objective contemplated in the original plan.

Another outstanding fact emerging from industrial development and research is that the use of more refined tools and more precise equipment, together with better control of experi-

* Presented at the American Physical Society Symposium on Physics in the Textile Industry held February 19–20, at Chapel Hill, North Carolina.



IDEALIZED STRUCTURE OF THE COTTON HAIR

The hair wall surrounding the central lumen or canal is pictured as made up of layers of cellulose in a growth-ring type of structure. These layers are further separated into segments or fibrils by pits which spiral around the length of the hair. It is estimated that 100 fibrils in each of 30–35 growth-ring layers constitute the wall, and moisture may adsorb on the four surfaces of each fibril as pictured. Swelling is conceived as being due to adsorbed layers of water molecules on the fibril surfaces between adjacent growth-ring layers. Moisture adsorbed on the pit wall surfaces of these fibrils contributes little if any to swelling.

mental conditions than seems absolutely justified, frequently unearth important evidence which might not be secured otherwise, or even anticipated. This fact is frequently overlooked, perhaps because investigators may be faced with the necessity of limiting experiments to the solution of practical questions of manufacture or for other reasons.

A change of but 1 percent in atmospheric relative humidity, equivalent to between 0.1 percent and 0.2 percent change in moisture content, causes a change of about 25 percent in the insulation resistance of cotton. With silk the corresponding change in resistance is somewhat greater, as this material is more sensitive to humidity changes than cotton. Since the electrical properties of textiles are so critically dependent on moisture content and humidity, in a study of these properties it is essential to have closer control of testing conditions than is usually found in textile laboratories. Perhaps the most important feature of the apparatus which has been developed for this work is the continuous absolute humidity recorder designed at our request by the Leeds and Northrup Company. It is sensitive to changes of but 0.05 percent relative humidity at room temperature, and is capable of measuring any atmospheric humidity from temperatures well below freezing to those above the boiling point of water. This recorder has been most valuable in conjunction with an apparatus capable of maintaining a continuous flow of air at such constant relative humidity that the recorder gives indication of but very small humidity variations over long periods. Fig. 1 is an example of this constancy.

The smallest divisions across the chart correspond to a relative humidity of 0.092 percent at 25°C, and for humidities below about 10 percent the relation between millivolt unbalance and humidity is substantially linear. The vertical divisions are time intervals of 45 minutes each. The record is for air at 3.96 percent relative humidity for a 16-hour period. The initial and final values for this air are identical, being $0.99 - 0.13 = 0.86$ millivolt and although a slight downward drift occurred followed by a return to the initial value it has been shown that this is due to changes during the night in the line voltage supplying current to the thermal conductivity cell. Even this small drift has been substantially eliminated by the proper ballasting of the line voltage supply. The total magnitude of this drift was 0.02 millivolt, a deviation of but 0.01 from the mean value, equivalent to a possible change of but 0.05 percent relative humidity for the 16-hour run. Further evidence of constancy was obtained in a continuous test on air at low relative humidity over a period of one week. Current adjustments were made but once a day and dry-air zero settings were taken but three times during the week. These dry-air zero settings differed by only 0.01 millivolt.

The recorder and associated humidity apparatus have proved useful also in the study of a wide variety of problems not related to textiles. As a matter of fact, the recorder itself was

designed for a thoroughly practical purpose, that of measuring atmospheric relative humidities (R.H.) between 0.1 percent and 10 percent at temperatures between 100° and 200°F, in heated storage ovens used in the manufacture of paper insulated telephone cables. Recorders of this type have been in commercial use for this purpose for more than 5 years and have given perfectly satisfactory service, even though they are essentially a research tool.

It is possible, with this apparatus, to provide any predetermined humidity for experimental tests within reasonably close limits, and to know, during the whole course of the experiment, that the humidity has undergone no substantial change. This has been highly important in connection with the interpretation of certain "by-product" results of our investigation of the electrical properties of textiles, and has helped

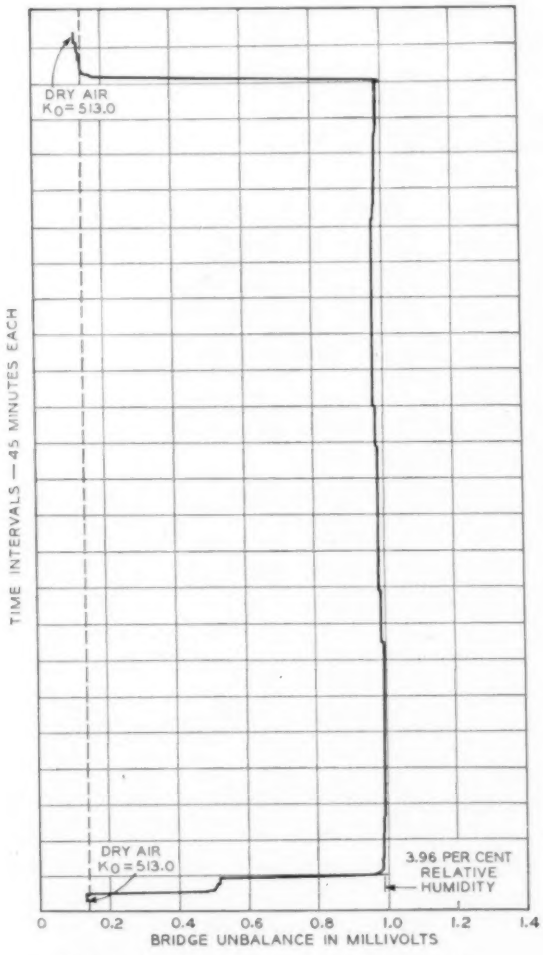


FIG. 1. Continuous record of low humidity.

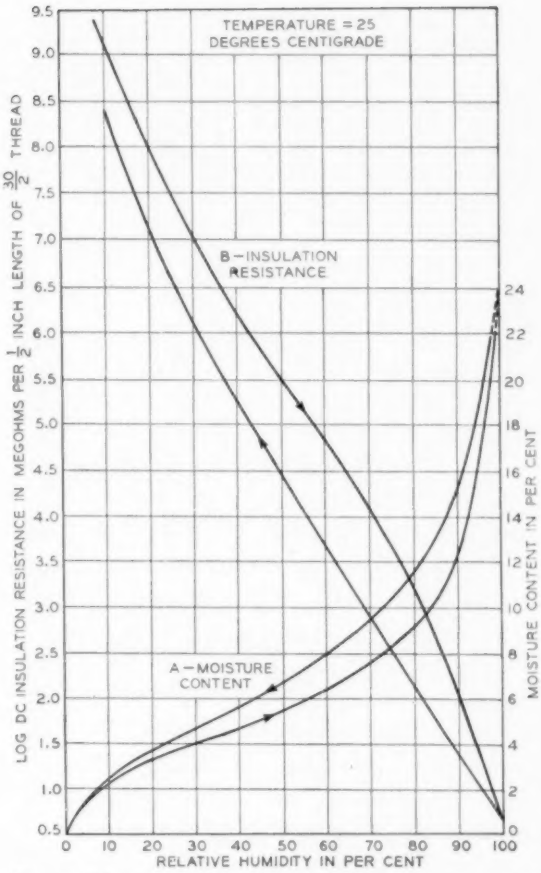


FIG. 2. Moisture adsorption and electrical properties of raw cotton.

to secure a better understanding of the mechanism of moisture adsorption in cotton and its effect on the physical properties of the material.

Electrical Properties of Cotton

Fig. 2A shows the familiar equilibrium relation between relative humidity and the moisture content of cotton. There is shown also on this figure the hysteresis loop which has been discussed at length by other investigators in recent years, notably Urquhart and Williams. The fact that there is a similar hysteresis characteristic in the relative humidity insulation resistance relation of cotton shown by Fig. 2B has been brought out in publications from our laboratories.[1, 2] Fig. 3 shows more clearly a fact, suggested by a comparison of the two types of curves in Fig. 2, that the resistance of cotton is critically dependent upon its moisture content (M.C.), since it is possible to derive a simple equation expressing this relation over a rather

TABLE I.

Sample No.	% Moisture Content 87.5% R.H.	84.3% R.H
1	10.95	10.1
2	10.8	10.0
3	10.7	9.9
4	10.8	9.8
5	11.1	10.2
6	11.0	9.9
7	11.8	10.8
8	10.7	10.1
9	10.85	9.8
10	11.0	10.0
11	10.7	9.9

wide range of atmospheric conditions, i.e.,

$$\log \text{Ins. Res.} = -A(\log \% \text{ M.C.}) + B. \quad (2)$$

The curves given in Fig. 3 show another important fact. The resistance of a cotton sample may have, not one, but a *range* of insulation resistance values for a single moisture content, depending upon the previous treatment or "history" of the sample.

A careful study of the implications of the relation shown in this figure has led to many improvements in methods now employed in the fundamental investigations of the electrical properties of textiles, and in inspection methods employed in the commercial purification of these materials for electrical purposes.

The behavior of cotton, as shown in Fig. 3, suggested that even if cotton is brought to the same atmospheric test condition from the same direction, to avoid hysteresis, and with presumably the same history, different samples might have different moisture contents. That such is the case may be seen from the following data: 11 samples of cotton, taken successively from the same spool, were dried to constant weight in a current of dry air, then equilibrated together under very carefully controlled conditions, first at 87.5 percent R.H.—100°F, and then several days later at 84.3 percent R.H. —100°F. The moisture contents of these samples are given in Table I.

The moisture contents of these samples showed small but definite differences, persisting even between tests several days apart. One of the samples had apparently been treated slightly differently in preparation since it preserved a marked difference in moisture absorption from the others. Incidently these samples had been thoroughly dried between the two tests above represented.

Since a difference of but 0.1 percent in moisture content may cause a difference of 25 percent in insulation resistance these data are considered significant in such testing methods as are used for electrical textiles.

The effect of drying temperature may be seen from the following test. Two samples of wet cotton were dried differently, one in an oven at 110°C, the other allowed to air-dry in the room. When tested as above, the air-dry sample gave 10.8 percent M.C., the oven-dried sample 9.85 percent.

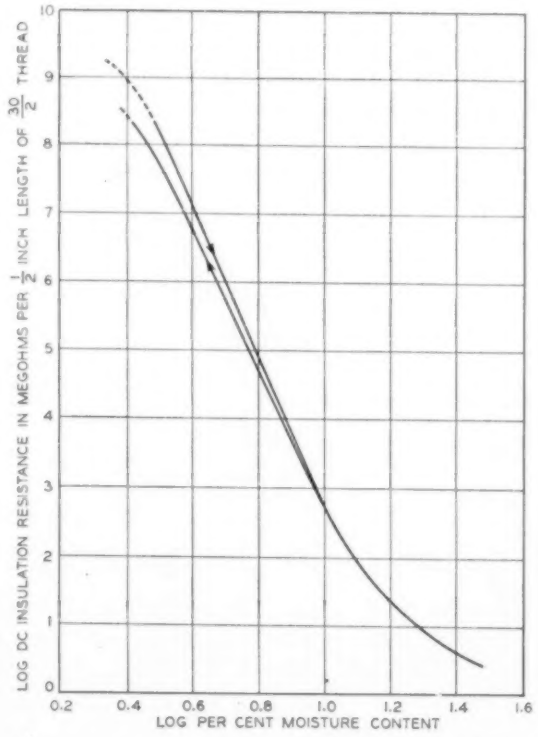


FIG. 3. Effect of previous history on insulation resistance of raw cotton.

Naturally Occurring Ash Electrolytes in Cotton

The ash of raw cotton is about 1 percent of its dry weight. This ash is composed principally of inorganic potassium and sodium compounds which exist as water-soluble salts in the cotton. The remaining ash constituents are more insoluble salts of calcium, magnesium, iron and aluminum. Washing of the cotton in water

removes substantially all of the potassium and sodium salts, and reduces the ash content to about one-fourth of its initial value. The I.R. of such washed cotton is from 10 to 100 times higher than the raw cotton, depending upon the method of drying. Bleaching or treating cotton with weak acids still further reduces the ash content, but adds little to its insulating quality. In fact, measurements made on fibers of "standard cotton cellulose," an extremely well-purified cotton* having an ash content of less than 0.1 percent gave insulating values comparable with fibers of water-washed cotton.

That these water-soluble salts conduct current through the cotton fiber structure by electrolysis is shown strikingly by a simple experiment, illustrated by the accompanying photographs.

When organic materials, containing small amounts of alkali salts, are ignited at a suitable temperature in a muffle furnace, these salts melt before the organic constituents are completely burned and spread as a glass-like coating over the partially carbonized material, leaving a blackened residue. A partially ignited raw cotton thread is shown in Fig. 4A. A similar thread, mounted between platinum electrodes and exposed to a high humidity, was polarized with direct current for a period of one week. On ashing this thread, the effect shown in Fig. 4B was obtained. Here the negative electrode portion of the thread shows as a large lump of carbonized material, protected with a glass-like coating which reacted strongly alkaline to indicators. This black lump trails off towards the center of the thread, first to a white ash, then to no ash at all, indicating migration not only of the readily water-soluble ash constituents, but also of the less-soluble material as well.

Fig. 4C shows another thread from this same experiment. In this case the potential had been removed at the time the thread in Fig. 5 was taken for ashing, leaving the remaining turns of thread about the platinum electrodes at high humidity for another week. The ash in Fig. 6 shows a remigration of the electrolytes back along the length of the thread.

That salts of the alkali metals, which melt at low temperature, are responsible for this effect is shown by Fig. 4D. The ash residue on the left is from raw cotton; that in the center from washed cotton; and that on the right from washed cotton dipped in dilute sodium hydroxide solution. All three were ashed simultaneously. The washed thread ashed readily to a white residue, retaining faithfully the outlines of the individual fibers composing the thread, when viewed under a microscope. The alkali treated cotton and the raw cotton look very much alike, showing the effect of low melting alkalies.

Distribution of Moisture in Cotton

In a previous publication[1] a series of simple equations were formulated to show the relation between moisture content, relative humidity, and the electrical insulation resistance of cotton;

$$\log \text{Ins. Res.} = -A(\%\ \text{M.C.}) + B, \qquad (1)$$

$$\log \text{Ins. Res.} = -A(\log\ \%\ \text{M.C.}) + B, \qquad (2)$$

$$\log \text{Ins. Res.} = -A(\%\ \text{R.H.}) + B. \qquad (3)$$

Eq. (1) was considered as representative of moisture contents below 3 percent, Eq. (2) for

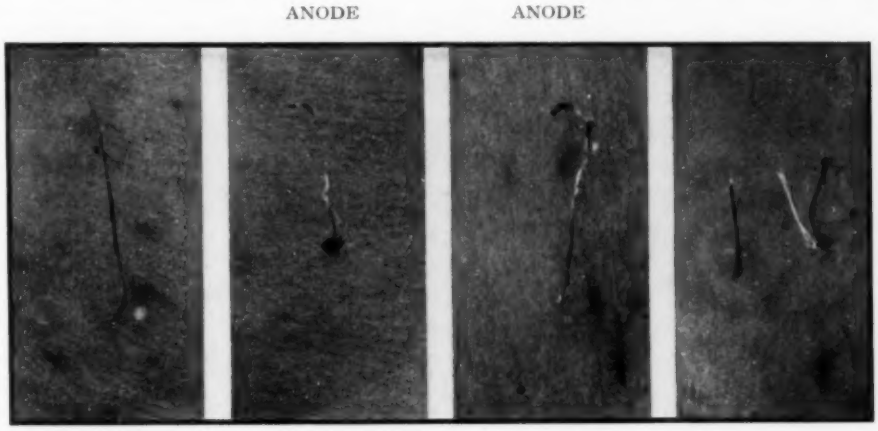


FIG. 4. Photomicrographs of ashed threads. (*A*) ash of untreated cotton, (*B*) ash of polarized untreated cotton, (*C*) ash of untreated cotton depolarized, (*D*) comparison of ashes of (left to right) untreated, washed, and subsequently treated cotton.

* "Preparation of Standard Cotton Cellulose," J. Ind. and Eng. Chem. **15**, 748 (1923).

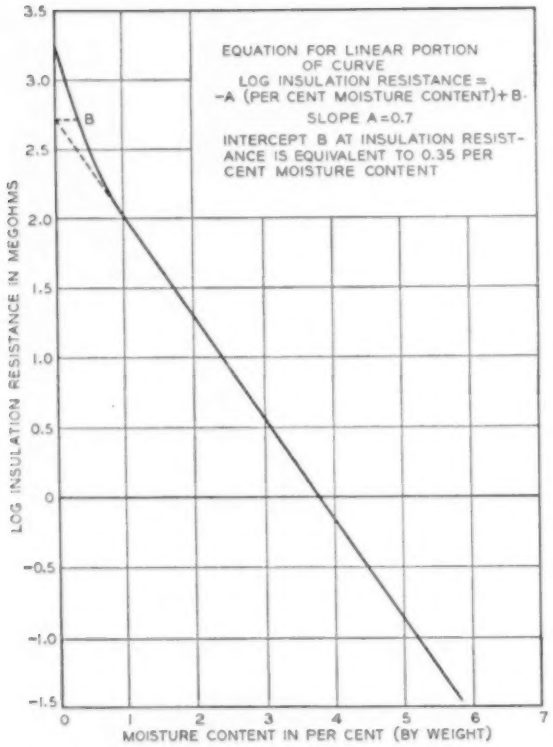


FIG. 5. Moisture content—insulation resistance relation for rag paper.

moisture contents between 3 percent and 10 percent, and Eq. (3) between 10 percent M.C. and saturation.

Since the resistivity of cotton becomes enormously high as the moisture content approaches zero, it has been difficult to extend the study of these relations much below 3 percent M.C. However, a recent study along somewhat different lines has provided us with information which gives valuable evidence on this relation down to as low as 0.04 percent M.C. The humidity recorder previously discussed was a most important factor in the success of this investigation.

The data are plotted on Fig. 5. Between 1 percent and 6 percent moisture content it will be seen that Eq. (1) holds. Below 1 percent moisture content, however, the resistivity increases more rapidly with decreasing moisture content than is consistent with Eq. (1).

These data complete a chain of evidence upon which is based a theory of moisture adsorption which appears adequate to explain many properties of cotton. Since the details of this theory are to be presented in a separate publication, only an outline will be given here to indicate a direction in which further experimental work may lead to a better understanding of the properties of textiles.

It is assumed that moisture first adsorbs on dry cotton on the outer hair surface, then penetrates by diffusion into cracks and pits seen, under the microscope, to spiral around the hair. It adsorbs on these pit walls, and since the hair swells appreciably in cross section, but hardly at all lengthwise, it is further assumed that moisture in these pits will penetrate along surfaces which lie concentric with the lumen, along layers similar to tree growth-rings. Less than 0.5 percent moisture is estimated as being necessary to form a monomolecular layer on pit walls and growth-ring surfaces. From independent data on moisture adsorption and swelling it is estimated that about 1 percent of water is required to cover all internal surface with a monomolecular layer, hence only a small part of this total is involved in the cross-sectional swelling of the cotton hair, and only about half of this total, that on pit walls and growth-ring surfaces, may be significant as providing moisture paths along which current is carried. This surface on pit walls and growth rings is termed fibril surface, in contrast to the further internal surface which possibly exists in the body of these so-called fibrils, and may be so located as to be responsible for the lengthwise swelling of the hair.

Furthermore it appears likely that each adsorbed water molecule in the monomolecular layer is held upon active points or zones on the surface, these points or zones being hydroxyl groups on the cellulose.

Below 1 percent moisture content, it appears reasonable to explain the very rapid increase in resistivity of cotton with decreasing moisture content as being due to discontinuities in the layer of water adsorbed on the fibril surfaces, since current is conducted largely through the moisture film. It is not to be concluded, however, that once a monomolecular layer is established on the surface, that the film is necessarily continuous. Reference to Fig. 6 suggests that there may be wider spaces present between water molecules on certain hydroxyls than between water molecules on other hydroxyls. Hence above 1 percent M.C. there may still be high resistance paths in

series with low resistance paths, and the resistivity of cotton is not simply related to moisture content, but is in accordance with Eq. (1).

As moisture builds up on these surface layers, it is conceivable that the mechanism is that of piling up increasing numbers of water molecules directly on top of the first layer, in the form of chains, each one extending out more or less vertically from the surface hydroxyl anchor. Such chains are pictured as causing the transverse swelling when adsorbed on the growth-ring surfaces. As these chains increase in length, the ends may exhibit an increasing magnitude of oscillation. With increasing humidity those chains most closely adjacent to one another may establish increasingly permanent contact, and the change in resistance is likely to be in accord with Eq. (1), for relatively small increments in moisture will be required to complete many paths between such adjacent molecules.

As the chains still further lengthen, complete contact is established between the adjacent chains and since larger increments of water may be required to complete paths between the more widely separated chains, the relation of Eq. (2) begins to assume more importance.

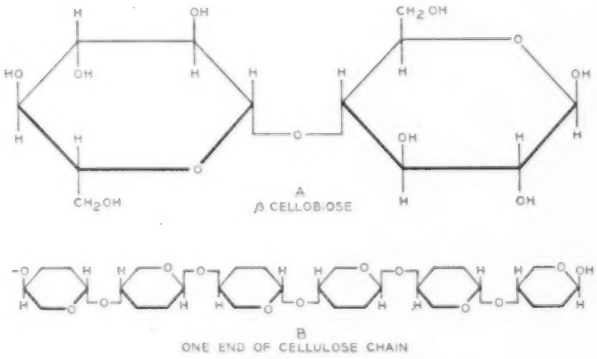


FIG. 6.

Finally as cotton approaches saturation the relatively high resistance due to current flowing through the lengths of tortuous paths of single water chains begins to be overshadowed by lower resistance paths in capillary condensed water, caused by lengthening chains effectively spanning the pits to an increasing depth. The insulation resistance thus appears to become more dependent upon vapor pressure, hence relative humidity, and Eq. (3) better expresses the relation between I.R. and M.C.

Based on this picture of moisture adsorption, it has been possible to calculate rather accurately the moisture content of cotton at any relative humidity, from swelling data. For example, at 50 percent R.H. the observed value is 5.4 percent moisture content. The estimated value is between 5.7 percent and 5.8 percent. Conversely swelling may be estimated from moisture content and humidity data.

This picture of moisture adsorption seems to provide a reasonable explanation for a variety of practical problems, for example:

It is known that if fibrous materials, such as wood, paper or fiber board are dried below a certain critical moisture content, permanent changes may be expected in the structure; even serious damage may result from too thorough drying at low temperatures. It seems evident that when the moisture content of such more or less dense structures is reduced to a point where the outer layers have less than 1 percent of moisture, the internal surfaces may begin to lose the monomolecular layer of water. The valence forces of surface hydroxyl groups, now no longer satisfied by water molecules, may be satisfied by other hydroxyls in the contiguous surface so that the surfaces stick together. On readsorption of moisture, portions of these surfaces may have become so permanently attached to one another that swelling will no longer occur in just the same way as originally, and cracking and warping may result.

A fabric dried by contact with a steam heated drum, without pressure ("can" drying), has a harsh feel, and is fairly stiff as compared with that dried by hot air. Furthermore, if a fabric is dampened to too great an extent before calendering (drying under both heat and pressure) it is apt to be thin and have a crisp, papery feel. This may be partially removed by swelling the fibers again through wetting, but it is said to produce a permanently undesirable effect. It is conceivable that some internal surface can be more or less permanently closed to moisture so that the material loses elasticity and becomes harsh, because of the lack of some lubricating moisture film between what were formerly internal surfaces.

During recent years much has been done to overcome the shrinkage problem in textile fabrics. Processes have been developed for applying predetermined amounts of shrinkage by mechanical means (Sanforizing) and this counteracts the inherent tendency of fabrics to shrink when laundered. This mechanical shrinkage has so far been applied almost entirely to cotton and linen, but wool still presents a difficult problem.

According to studies made at the Shirley Institute, shrinkage which commonly occurs on wetting and drying a fabric may be divided into three parts, (a) fiber shrinkage, (b) yarn shrinkage, and (c) increase of crimp.

(a) is important in the case of woolen cloth. It has been shown by Astbury[3] that the molecular structure of wool may be likened to linked chains of coiled springs. These tiny molecular springs explain the great elasticity of the wool fiber. They are tightly coiled when not subjected to external strains, but can be stretched as much as 100 percent from which extension they will rapidly recover, unless "set" by special treatments, such as steaming for a short time and then drying under tension. On wetting again, this "set" is released and the fibers contract, but unfortunately, they may be either longer or shorter than the original length, thus increasing the difficulty of compensating for undesired shrinkage by mechanical means.

Cotton fibers, on the other hand, exhibit no such marked "set," showing not more than one to two percent. Both wool and cotton, however, are affected by (b) and (c). The yarn shrinkage of cotton is simply that due to swelling of the fiber, so that each one of which a yarn is composed requires more room, with the result that the yarn diameter is increased. The fibers are coiled spirally around this larger diameter, hence cannot span so far along the yarn as formerly, so that the yarn contracts in length. Wool yarn also exhibits this behavior, but in addition, wool exhibits the property of felting, so that when vigorously rubbed or scrubbed in washing, the fibers slip past one another, further increasing the shrinkage. This felting factor is not entirely reversible, nor is it constant in amount, consequently it is evident that the complexity of the behavior of wool would make it difficult to estimate preshrinkage quantitatively.

Since it has been shown in this paper that very close estimates may be made of cotton moisture content from swelling data, or conversely that the swelling of cotton at any humidity can be computed from moisture content data, it is not surprising that a predetermined amount of shrinkage may be successfully applied in the manufacture of cotton cloth.

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3. W. T. Astbury, *Fundamentals of Fiber Structure* (Oxford Press, 1933), p. 96.

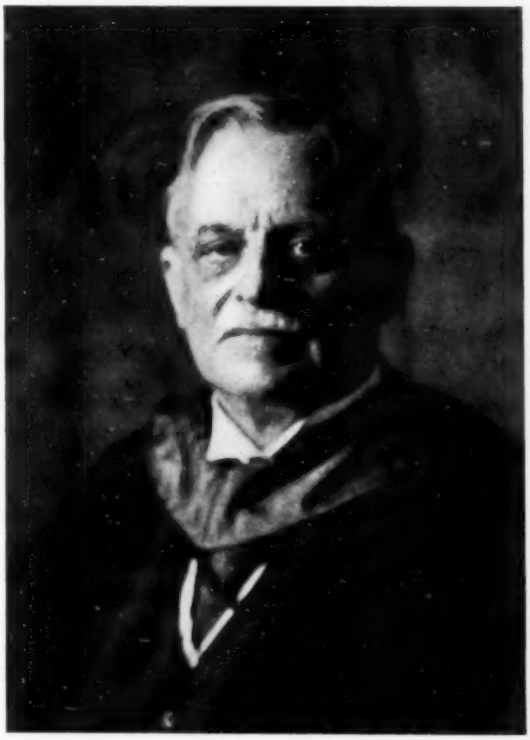
If industrial research were done by more and better people, we should have less unemployment and perhaps none. This is perfectly obvious. There is, and always will be, an increasing circumference of untested assets about us and an infinitely fertile area for progress just adjacent to the known.—W. R. WHITNEY.

Elihu Thomson

Professor Thomson's loss would be irreparable were it not for the fact that his nobility of character will remain as a lasting inspiration and his scientific achievements will continue permanently to confer immeasurable benefits to the world.

—KARL T. COMPTON

PROFESSOR ELIHU THOMSON, 83, dean of American scientists, and one of the founders of the General Electric Company, died at his home in Swampscott, Mass., March 13. He had been seriously ill since January. Professor Thomson, together with Thomas A. Edison, James J. Wood, and Charles F. Brush, were the great quartet which created the modern electrical industry. Funeral services were conducted in Lynn, Mass.



Elihu Thomson was one of America's greatest pioneers in the field of electrical science. His technical work was directly reflected in practical developments, as he was one of the most farsighted of the early arc-light inventors, and experimented with the principle of alternating-current transmission far in advance of commercial demands. He held upward of 700 patents in the United States alone.

He originated the resistance method of electric welding, which has been in continuous use from 1887 to the present time; developed the repulsion type of induction electric motor; invented the magnetic blow-out principle in lightning arresters and electric switches, the oil-cooled type of transformer, the constant-current transformer, and the modern process of commercially treating fused quartz.

Professor Thomson's name was given to the Thomson-Houston Electric Company, organized in 1883, and merged in 1892 with the Edison General Electric Company to form the General Electric Company of today. He has ever since been associated with General Electric and at the time of his death was dean of that company's staff of scientists. For more than 15 years he was director of the Thomson Research Laboratory, located at the River Works of the Company at West Lynn, Mass.

There was scarcely any aspect of electrical science in which Thomson had not been active at some time or another. More than 10 years before Hertz in Germany discovered the electromagnetic waves of radio Thomson was demonstrating, in 1875 at Philadelphia, the transmission of signals without wires. He originated the three-phase electric dynamo machine in 1879 and anticipated experimentally, in the same year, the modern practice in transformer work. He invented the first practical wattmeter, thereby winning half of the grand prize offered at the close of the Paris electrical exposition of 1889.

Outside of electrical matter he was also active. He invented the centrifugal cream separator and the centrifuge, an instrument now universally used in biological laboratories. He also devised the fluid pressure engine and the fused quartz mirror for astronomical telescopes. On this latter development he made many important contributions.

His lifetime hobby was astronomy, in which he was active as an amateur at an early age. He was also interested in microscopes, autochrome photography, and in building and playing pipe organs. He had a host of friends in scientific and engineering circles, not only in America but in Europe, particularly in England, the land of his birth.

Professor Thomson was the only man who ever received all three of England's highest scientific honors—the Hughes, the Lord Kelvin, and the Faraday medals. He also had the medal of the Verein Deutscher Ingenieure, outstanding German engineering award, the John Fritz medal from the four leading American engineering societies, and the medals of the Franklin Institute, the American Academy of Arts and Sciences and the American Institute of Electrical Engineers. He was president of the International Electrical Congress in 1904, and the president of the Electrochemical Congress in 1910 and 1911. At one time he was vice president of the American Academy of Arts and Sciences and vice president of the American Philosophical Society. He belonged to innumerable engineering societies all over the world.

Here and There

¶ Professor A. A. Atkinson, for a number of years head of the department of electrical engineering at Ohio University, Athens, has been appointed dean of the College of Applied Science, which includes the departments of electrical, civil and industrial engineering, industrial arts, agriculture and the School of Home Economics. Dr. W. S. Gamertsfelder, professor of philosophy, has been made dean of the College of Arts and Sciences and of the Graduate College, succeeding Dean E. W. Chubb, who retired recently.

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¶ Dr. Arthur Holly Compton, Nobel Prize winner and professor of physics at the University of Chicago, delivered an address entitled "We Must Shape Our New World," over the NBC-Red Network at 4:15 p.m., EST, Easter Sunday, March 28.

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¶ Charles E. McQuigg, since 1934 director of research of the Union Carbide and Carbon Corporation, New York City, has been appointed dean of the College of Engineering of Ohio State University. He succeeds Emeritus Dean Embury A. Hitchcock, who retired last July.

★

¶ The James F. Lincoln Arc Welding Foundation announces a contest to encourage and stimulate scientific interest and research in the development of the arc welding industry through advance in the knowledge of design and practical application of the arc welding process. The Foundation will make awards, by prizes, to those persons who by reason of the excellence of their papers upon said subject may be selected in the manner provided by the rules as most worthy to receive such awards. In order to stimulate the greatest study of arc welding, this contest embraces practically every field of industry where arc welding can be applied as a primary process of manufacture, fabrication or construction. A total of 446 prizes are provided for papers in this contest. From 44 subclassifications, 220 papers will be selected to receive prizes totaling $81,400. From the 220 papers receiving prizes in the subclassifications, 44 papers will be selected to receive prizes totaling $74,800 in the main classifications. From the 44 papers receiving prizes in the main classifications, papers will be selected to receive the four main contest prizes totaling $26,000. In addition 178 prizes of $100 each are provided for papers which do not share in any other award but which in the opinion of the Jury of Award deserve Honorable Mention. These may be selected from any classification. The winner of the Grand Prize for the contest will receive $13,700. He will receive the First Prize of $10,000 for the contest, the First Prize of $3,000 for his main classification and the First Prize of $700 for his subclassification.

All communications relative to the contest shall be addressed "Secretary, The James F. Lincoln Arc Welding Foundation, P. O. Box 5728, Cleveland, Ohio."

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¶ Dr. Paul D. Foote, executive vice president of the Gulf Research & Development Company, spoke on February 25th at a meeting tendered the students and staff of Massachusetts Institute of Technology by the local chapter of Sigma Xi. His talk on "Recent Trends in Petroleum Research," illustrated with still and moving pictures, gave a general review of the research problems in various branches of the petroleum industry.

New Industrial Fellowships

¶ President Karl R. Compton announces a new educational program at Massachusetts Institute of Technology. Fifteen fellowships (stipends of $1450 single and $1950 married) will be awarded to technically trained young men in business and industry who show exceptional executive promise, intellectual capacity and physical resource. The fellowships will be for a full year and under the direction of Professor Erwin H. Schell, head of the department of business and engineering administration, with the aid of an advisory committee of educators and executives.

Those receiving these honorary fellowships will begin in June a twelve months' leave of absence from their employers. Their studies will start with courses in production, marketing, finance, accounting, business law and industrial relations. They will live together and their training will include administrative seminars, weekly conferences with distinguished business and industrial administrators and original research.

As a special advisory committee on the new program of Honorary Fellowships in Business and Engineering Administration a distinguished group composed of Dr. A. Lawrence Lowell, former president of Harvard University; President Frank Aydelotte of Swarthmore College; The Reverend Leslie Glenn, Rector of Christ Church, Cambridge; Edmund C. Mayo, President of the Gorham Manufacturing Company, and President Karl T. Compton of M. I. T. has been appointed.

★

National Geographic Society—U. S. Navy Eclipse Expedition

¶ The National Geographic Society and the U. S. Navy will send a joint expedition to observe the total solar eclipse of June 8 to the Phoenix Islands in the mid-Pacific Ocean just south of the Equator about 1,800 miles southwest of the Hawaiian Islands. The expedition will establish itself upon either Canton or Enderbury Island, which are the only two islands of the eight in this group near enough to the center of the band of totality to afford satisfactory conditions for observation. No other island from which satisfactory observations can be made is to be found within the entire 8,800 miles of the path of totality extending from near the New Hebrides to the coast of Peru. Choice between Canton and Enderbury Islands will be made after the expedition arrives in the locality and observes which island offers the best facilities for a camp.

The personnel of the expedition is as follows: Dr. S. A. Mitchell, director of Leander McCormick Observatory, University of Virginia, scientific leader; Captain J. F. Hellweg, superintendent of the U. S. Naval Observatory, who will have charge of the Navy's participation; Dr. Paul A. McNally, director of Georgetown College Observatory; Dr. Floyd K. Richtmyer, of Cornell University; Dr. Irvine C. Gardner, National Bureau of Standards; Dr. Theodore Dunham, Mt. Wilson Observatory; Richard H. Stewart, of the staff of the National Geographic Society; John W. Willis, U. S. Naval Observatory; and an engineer of the National Broadcasting Company.

Special attention will be devoted to observations of the sun's corona and the chromosphere. Dr. Mitchell will observe the flash spectrum which becomes visible during the few seconds just after the moon completely covers the sun and just before the sun begins to emerge again.

Dr. Mitchell and Dr. Dunham will use three powerful spectrographs to photograph the spectrum of the chromosphere and that of the corona. Each instrument will consist of a concave grating used without slit. All of the gratings are of six inches aperture and ruled with 15,000 lines per inch. The two gratings used by Dr. Mitchell will be of 10 feet radius of curvature, giving a dispersion of 10.9 angstroms per mm. He will employ the technique always followed in his nine previous eclipse expeditions of photographing on a fixed plate with rapid changes between exposures.

Dr. McNally will photograph the corona with two cameras on an equatorial mounting driven by clock work. Assisted by Mr. Willis, he also will photograph the corona with a 15-foot horizontal camera into which the light of the sun will be fed by a coelostat mirror. Dr. Gardner will use a camera of his own design of nine inches aperture and 19-foot focal length with which in the U. S. S. R. he obtained successful black and white and color photographs of the eclipse of June 19, 1936.

FLOYD K. RICHTMYER

Photographs of the spectrum of the corona will be undertaken by Dr. Dunham using a very fast spectrograph. Dr. Richtmyer will measure visually the total light of the corona for comparison with the radiation from the full moon and will also measure the percentage of polarization at different distances from the sun's edge.

Accurate timing of the contacts of the edges of the sun and moon, particularly the second and third contacts marking the beginning and end of totality, will be undertaken by representatives of the Naval Observatory. This will be done both visually and photographically, all times being recorded upon a chronograph. Time signals will be available by radio and special time signals probably will be broadcast from Honolulu to the island on the day of the eclipse.

It is planned tentatively to observe the effect of the eclipse upon the ionosphere, a very definite effect having been noted during the total solar eclipse of 1932.

A description of the eclipse will be broadcast from the island and sent over the nationwide network of the National Broadcasting Company and rebroadcast to foreign countries.

Because of the nearness of the eclipse date to the sunspot maximum in 1939 it is expected that the corona will be nearly circular in shape and that there will be a large number of prominences, since the surface of the sun is highly excited during a time of increasing sunspots.

¶ Cornell University announces a symposium on "The Structure of Metallic Phases" to be held in Ithaca, N. Y., early this summer. The discussions will center around cooperative phenomena such as allotropy, superstructures, and ferromagnetism from both theoretical and experimental points of view. The complete program will be announced in a future issue of this journal.

★

¶ The American Institute of Electrical Engineers announces that Dr. Frank Conrad will be presented its Lamme Medal at the summer convention in Milwaukee, June 21–25. Dr. Conrad is associated with the Westinghouse Electric and Manufacturing Company. Among his research developments are improvements in arc lamps, automobile ignition systems, mercury vapor rectifiers, radio telephony, telegraphy, electric clocks, measuring instruments for both alternating and direct current. He holds more than 200 patents. Dr. Conrad has previously received other honors: the Morris Liebmann prize for 1925 of the Institute of Radio Engineers, the Edison medal of the American Institute of Electrical Engineers for 1930 and the John Scott medal of the City of Philadelphia in 1933.

★

¶ On March 9, 1937, Dr. K. E. Corrigan, physicist at Harper Hospital, gave an illustrated lecture to the Detroit Physics Club on "The Applications of Modern Physics to Medical Research." The meeting was held in the Harper Hospital amphitheater, after which the 500,000 volt x-ray tube was placed on display.

★

¶ The Association of Illuminating Engineers (France) communicates that, at the occasion of the 1937 Paris International Exposition, an *International Congress devoted to Lighting Applications* will take place in Paris between June 24 and July 1. General reports and private communications will be presented on the following questions: Luminous sources, Luminaires, Street and road lighting, Lighting of festivals and expositions, Medical and surgical lighting, Industrial lighting (special applications), Natural lighting, Decorative lighting of interiors, and Outdoor decorative lighting.

Anyone who wants to participate or to obtain the Congress regulations, can write directly to the organization of the *International Congress of Lighting Applications, Paris 1937, 12 Place de Laborde, Paris 8° (France).*

★

American Ceramic Society

¶ The thirty-ninth annual meeting of the American Ceramic Society was held March 21–27 at the Hotel Waldorf-Astoria in New York. There was much of interest at this meeting for those who are applying physics. There were papers on the surface tension, elastic properties, x-ray diffraction analysis, photoelastic studies and specific refractivity of glass. In the white wares division there were papers on high temperature measurements and upon the physical basis of color specification.

¶ Dr. W. F. G. Swann delivered the annual James Arthur Lecture on "What is Time?" Friday, April 9, 1937, in the auditorium of the Gould Memorial Library, New York University. This lecture is one of the series entitled "Time and its Mysteries," which has been endowed by the late James Arthur. Mr. Arthur assembled one of the largest and most comprehensive historical collections of clocks and watches in existence which he presented to the New York University.

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¶ Dr. W. D. Coolidge and Dr. Irving Langmuir, director and associate director, respectively, of the General Electric Research Laboratory in Schenectady, and Dr. Evarts A. Graham of the School of Medicine of Washington University in St. Louis, were recipients of the John Scott 1937 awards granted by the City Trusts of the City of Philadelphia, March 5. With each award went a certificate, a copper medal, and $1000 in cash. The award to Dr. Coolidge was based on his application of a new principle in x-ray tubes; to Dr. Langmuir for his physical and chemical discoveries resulting in improved gas-filled incandescent lamps; and to Dr. Graham for his application of the x-ray to the study and diagnosis of gall bladder conditions.

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¶ The new laboratory of the Mellon Institute of Industrial Research of Pittsburgh will be dedicated formally, May 6, 1937. This laboratory replaces the older one which has been in use for twenty-two years. It is to be dedicated in the presence of many eminent scientists in honor of Andrew W. and the late Richard B. Mellon, who founded the Institute in 1913. On May 7, a symposium on recent progress in science is to be held.

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¶ The National Research Council announces a tour this summer of European research laboratories by a group of industrial and banking executives, from all sections of the United States. The tour, planned by the National Research Council's Division of Engineering and Industrial Research, will enable the group to visit scientific and industrial research laboratories in England, Germany and France representing eighteen different fields of industry, and laboratories of governments, universities and trade associations will also be visited. European hosts will be such organizations as the Department of Scientific and Industrial Research in England, the Verein Deutscher Ingenieure in Germany, the Sorbonne in France, and others, according to Maurice Holland, director of the Division.

The purpose of the tour is to acquaint industrial keymen of this country with developments and methods in the leading industries of Europe. Mr. Holland, who during the past fifteen years has been visiting all those countries of the world where industry has made strides, will be in charge of the tour. Travel arrangements are being made by American Express, and according to preliminary plans, the group will sail from New York, May 14, on the S. S. Champlain. Approximately one hundred bankers and industrialists are expected to participate.

Instrument Booklets Received Recently

Radiation Measuring Apparatus (3 pp.). A simple radiation measuring apparatus is described. It consists of a thermopile which is provided with a tube containing diaphragms and a double walled shutter. The thermopile is connected to a galvanometer placed in a portable case fitted with a lamp and a scale.

Moll Colorimeter and Nephelometer for the objective measurement of the turbidity and absorption (4 pp.).

Recording Spectrometer for the quantitative analysis of spectra in the infrared, visible and the ultraviolet. It gives directly and automatically a curve relating spectral energy and wave-length (4 pp.). The above booklets are all obtainable from P. J. Kipp & Zonen, Delft, Holland.

The General Radio Experimenter, January 1937. In this issue are described the measurement of mutual inductance and new types of wave filters.

Moll Recording Microphotometers. In this 12-page booklet are given the optical and mechanical arrangements of the Moll Recording Photometer. Samples of the microphotometer records of hyperfine structure of cobalt and the spectrum of copper are obtainable from P. J. Kipp & Zonen, Delft, Holland.

Among Our Authors

W. H. HANSEN

Professor William W. Hansen's brother is an artist and we have him to thank for this excellent sketch. Dr. Hansen was born in 1909 at Fresno, California and received his A.B. and Ph.D. from Stanford University. He held a National Research Council Fellowship at Massachusetts Institute of Technology and at the University of Michigan 1933–34. Since 1934 he has been Assistant Professor of Physics at Stanford University.

R. N. TRAXLER

Dr. R. N. Traxler was born at Lamar, Colorado in 1897. He received his bachelor's degree at Colorado and his Ph.D. from Wisconsin. Since 1929 he has been Chief of the Research Division of The Barber Company, Inc., Maurer, New Jersey.

Dr. J. D. Cobine was born in 1905 at Oklahoma City, Oklahoma. In 1931 he received his B.S. degree in Electrical Engineering from Wisconsin and subsequently his M.S. and Ph.D. from California Institute of Technology. He is now an instructor at the Harvard Graduate School of Engineering.

J. D. COBINE

Mr. Charles Edwin Coombs was born at Holyoke, Mass., December 8, 1912. He received his B.S. at the Massachusetts State College in 1934 and his M.S. at Lafayette College in 1935. He is now occupied with Cellophane research at the E. I. du Pont de Nemours and Co. at Buffalo, N. Y.

C. E. COOMBS

R. B. POWER, JR.

Mr. R. Burton Power, Jr., was born in 1911 at Lawrence, Kansas. He has his bachelor's degree from Kansas, M.S. in Electrical Engineering from Harvard, and is a candidate for S.D. from Harvard in June. At present, he is with the Kennecott Wire and Cable Co., Phillipsdale, R. I.

Contributed Original Research

The Flow of Fluids Through Porous Media*

MORRIS MUSKAT
Gulf Research & Development Company, Pittsburgh, Pennsylvania
(Received January 6, 1937)

THE title of this paper might suggest that it consists of a discussion of some new solutions of the Stokes-Navier differential equations forming the basis of the classical hydrodynamics. For the academic instruction of physicists usually leaves the student with the impression that the subject of the hydrodynamics of viscous flow is completely described by the Stokes-Navier equations, and that all that is necessary for the treatment of a specific problem is the solution of the corresponding specialization of the equations. And indeed so the situation really is in a strict literal sense, even for the problem of the flow of fluids through the multiply connected passages of a porous medium.

However, from the point of view of practical expediency it is far simpler to begin anew from direct empirical observations and reconstruct the hydrodynamics appropriate to systems involving porous media than to attempt to use the old foundations and concentrate merely upon the analytical work of the solution. Any one who recalls the extreme simplicity of the problems that were used to illustrate the classical hydrodynamics in his first introduction to the subject or even those who have waded through the deep channels of Lamb's classical treatise, will readily agree that only the most extreme optimist would venture to derive a strict solution of the Stokes-Navier equations even for the slow motion of an incompressible liquid through the pores of a porous medium.

Although attempts to solve the problem of the flow of fluids through porous media by the classical hydrodynamics thus appear to be futile, it is natural to ask before undertaking a new attack if the problem is really of practical importance. Here the answer is quite simple and unambiguous. For the whole field of ground water hydrology including the provision and maintenance of water supplies, the scientific solution of irrigation problems, and efficient development of drainage systems is clearly only an application of the general theory of the flow of liquids through sands. The efficient construction of filter beds and the predictions of their properties by the sanitary engineer requires an understanding of the same basic principles. The seepage of water through, underneath, and around dams demands that the civil engineer be well versed in the fundamental bases of the flow of fluids through sands. The ceramic engineer must be familiar with this theory when studying the diffusion and the flow of fluids through ceramic materials such as bricks and porous earthen ware. And obviously the petroleum engineer, who is concerned with the production of gas and oil from underground reservoirs, has to have a thorough understanding of the mechanics of fluid flow through sands to be able to supervise the development of his property so as to obtain a maximum and most profitable recovery of the petroleum fluids.

It is clear therefore that there is good reason to venture forth boldly and attack the problem by direct empirical methods rather than to give up simply because the mathematician has not been able to derive the solution of the Stokes-Navier equations for the geometric system

* The subject of the flow of fluids through porous media has grown so rapidly in the last few years that only the barest outline of its foundations and several specific examples could be presented here. A comprehensive treatment of the subject will be published soon by the author in book form.

defined by the interior of a porous medium. This direct step was first taken by H. Darcy[1] in 1856, who was actually concerned with one of the problems mentioned above, namely, the flow of water through filter beds. At once he found the beautifully simple result that the flow of water through his filter bed was simply directly proportional to its cross-sectional area and to the driving head, and inversely proportional to the thickness of the bed. Or, in analytic form, he established the equation

$$Q = cA\Delta h/L, \tag{1}$$

Q being the rate of flow, A the cross section of the filter bed of thickness L, Δh the head of water inducing the flow, and c a constant peculiar to the sand constituting the bed. Now that this result is available, it will be quickly recognized that it bears a close resemblance to the Poiseuille law for the flow of liquids through a capillary tube. And indeed it might appear reasonable to assert that Darcy's law could have been anticipated on the basis of Poiseuille's law. However, it is safe to say that a rigorous demonstration of the existence of this bridge between Darcy's result and Poiseuille's law will remain only as an intuitive conviction even for many years to come.

The application of Darcy's result to the other manifold problems in which the same fundamental physical processes are involved requires that it be generalized. On the basis of both direct and indirect empirical evidence it has been found that it may be generally expressed in the form now know as Darcy's law, namely

$$\mathbf{v} = -\frac{k}{\mu}\nabla p, \tag{2}$$

where $\mathbf{v}$ is the vector fluid velocity, p the fluid pressure, μ the viscosity of the fluid, and k the constant characterizing the porous medium, and designated as its "permeability." Although this equation is the foundation of the whole subject of the flow of fluids through porous media, it should be understood that it is not an analytical solution of the Stokes-Navier equations derived empirically. Rather it represents only the macroscopic resultant of such solutions in which the dynamical quantities $\mathbf{v}$ and p are to be considered as statistical averages over a great number of pores. In fact, $\mathbf{v}$ is not even a physical velocity, but is simply the volume fluid flux per unit macroscopic area of the porous medium.

The importance of this law demands that its validity be carefully investigated. Reversing the above interpretation of Darcy's equation so as to state that the pressure differential is proportional to the fluid velocity, and noting that dimensional theory demands only a functional relation between pressure drop and the velocity, it is seen that the equation might be considered as representing only the first term in a Taylor's expansion of the pressure drop in powers of the velocity. And indeed this has been proposed by some investigators who have attempted to express the pressure drop in the linear column as binomials or even trinomials in the velocity. Of course some of these have proposed terms in the velocity raised to a fractional power, but little significance need be attached to such extremes of empiricism. A review of the available literature leads to the result that although for high velocities of flow the quadratic term may be justifiably added to the relation between the pressure differential and the velocity, the single linear term may be considered to be valid for all practical purposes in the low velocity region. As typical evidence we may cite Fig. 1 in which a great variety of data have been plotted in the form of a friction coefficient *versus* an effective Reynolds number, the unit slope of the curves indicating the validity of Darcy's law.[2] This will be obvious when it is noted that the friction coefficient is defined as the quantity $d\Delta p/2L\gamma v^2$ and the Reynolds number as $R = dv\gamma/\mu$, where d is the average grain diameter, Δp the pressure drop over the length L, and γ the fluid density, by analogy with the standard notations of hydraulic engineering. It will be noted that the deviations from a unit slope become noticeable only as R exceeds the value 1. Typical evidence of the justification for the quadratic term is indicated in Fig. 2 in which data are plotted that were obtained on the flow of air through a

[1] H. Darcy, *Les fontaines publiques de la ville de Dijon* (1856).

[2] These curves are taken from the paper by G. H. Fancher, J. A. Lewis, and K. B. Barnes, Bul. 12, Mineral Ind. Expt. Station, Penn State College (1933).

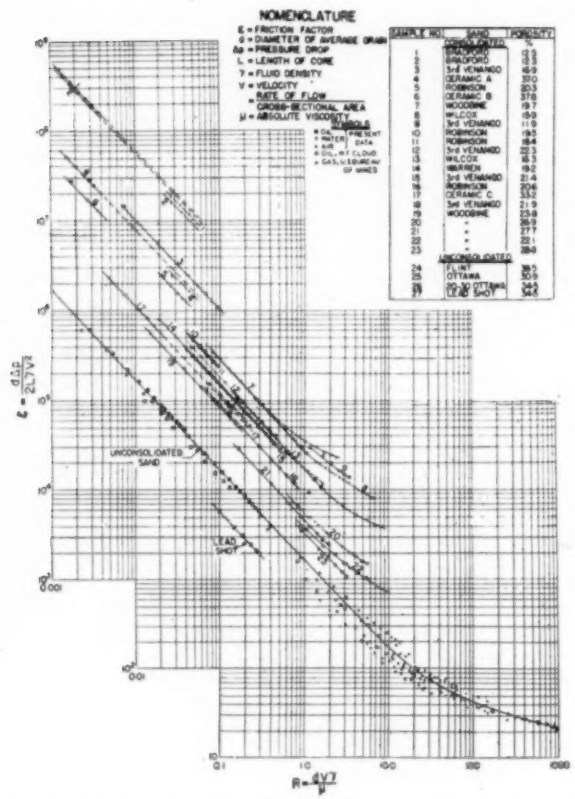

FIG. 1. Friction factor chart for the flow of fluids through sands (after Fancher, Lewis, and Barnes).

column of glass beads. The linearity of the curve for the larger values of the mass velocity is evidence of the quadratic relation between the pressure differential and the velocity, the significant variables here being the difference in the squares of the pressure and the mass velocity since the fluid is a gas. The break for low values of mass velocity corresponds to a change to a type of flow obeying Darcy's law, that is, in which the quadratic term is absent. The significance of the quadratic term is that it implies the presence of turbulence in the flow, as is the case in ordinary hydraulics where the fluid passes through an open conduit.

Summarizing, it may be said that Darcy's law will be valid when the Reynolds number is of the order of or less than 1. And it is important to note that this range covers almost all systems of practical interest except gas wells flowing at high rates where turbulence may develop within the immediate vicinity of the well bore. Furthermore it may also be noted that even in such cases where there may be some turbulence one is justified in approximating the flow by Darcy's law simply because the use of the more accurate quadratic expression would make it impossible to carry through the analysis giving the detailed characteristics of flow systems that are other than those of extreme geometrical simplicity.

As previously stated, Darcy's law is the empirical substitute for the Stokes-Newtonian hypothesis that the viscous frictional forces $(\mu\nabla^2\mathbf{v}+\frac{1}{3}\mu\nabla\theta)$, θ being the rate of volume dilatation of the fluid. The remaining elements of any hydrodynamic formulation, namely, the equation of state of the fluid and equation of continuity, must, of course, be the same here as in the classical hydrodynamics. Applying these to Darcy's law one then readily gets as the final equivalent of the Stokes-Navier equations for homogeneous fluids the following:

Incompressible liquids:

$$\nabla^2 p = 0, \tag{3}$$

Compressible liquids: $\gamma = \gamma_0 e^{\beta p}$,

$$\nabla^2\gamma = \frac{f\beta\mu}{k}\frac{\partial\gamma}{\partial t}, \tag{4}$$

Gases: $\gamma = \gamma_0 p^m$,

$$\nabla^2\gamma^{1+m/m} = \frac{(1+m)f\mu\gamma_0^{1/m}}{k}\frac{\partial\gamma}{\partial t}, \tag{5}$$

where β is the compressibility of the liquid and f the porosity—fractional pore space—of the porous medium.

In order to get a clear understanding of the meaning of these equations we shall illustrate them by application to several simple examples of practical interest. The first will be that of the production capacity of a well piercing a uniform horizontal sand saturated with an effectively incompressible liquid. If complete radial symmetry is assumed, Laplace's Eq. (3) for the pressure distribution reduces to an ordinary equation in the radial coordinate, with the solution

$$p(r) = \frac{p_e - p_w}{\log r_e/r_w}\log\frac{r}{r_w} + p_w, \tag{6}$$

where p_e, p_w are the boundary pressures at the boundaries r_e, r_w. The flux through the system,

or production capacity, is then given simply by

$$Q=\frac{2\pi kh}{\mu}\frac{\partial p}{\partial r}=\frac{2\pi kh(p_e-p_w)}{\mu \log r_e/r_w}, \qquad (7)$$

where h is the sand thickness.

These results are, of course, completely analogous to those for the electrical problem of the cylindrical condenser. For this case of extreme geometrical and physical symmetry it would hardly have been necessary to construct a general formulation of the problem of liquid flow through porous media. However, when the practical question is raised that in actual field conditions the pressure over a circular boundary concentric with the well surface will not be strictly uniform, one must appeal to a more general analysis in order to obtain the production capacity of wells in such cases. Here the solution may be derived in the following manner. It is supposed to begin with that the pressure distributions $p_w(\theta)$ over the well surface, defined by $r=r_w$, and the external boundary pressure $p_e(\theta)$, over the boundary $r=r_e$, are not uniform and

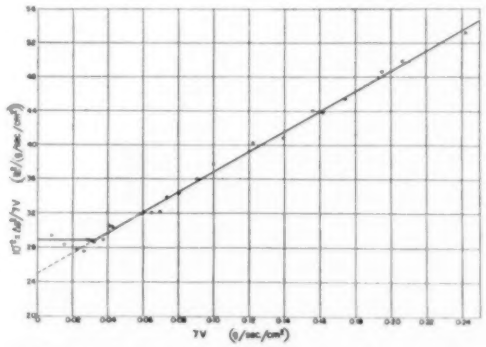

FIG. 2. Flow curves for air through uniform glass beads of 0.0632 cm diameter. Δp^2 = difference in squares of terminal pressures. γv = mass velocity. Break corresponds to $R\sim 10$.

that they may be resolved in Fourier series into the expressions

$$\left.\begin{aligned} p_w(\theta)&=\sum(w_n \sin n\theta+x_n \cos n\theta)\\ p_e(\theta)&=\sum(e_n \sin n\theta+f_n \cos n\theta)\end{aligned}\right\} 0\leqslant\theta\leqslant 2\pi, \qquad (8)$$

θ being the polar angle. A solution of Laplace's equation is then taken in the form:

$$p(r,\theta)=c_0 \log r+\sum r^n(a_n \sin n\theta+b_n \cos n\theta)+\sum r^{-n}(c_n \sin n\theta+d_n \cos n\theta). \qquad (9)$$

Proceeding now to adjust the coefficients a_n, b_n, c_n, and d_n so as to satisfy the boundary conditions, it is readily found among other relations that: $c_0=(f_0-x_0)/\log r_e/r_w$. It is now noted that the average values of $p_e(\theta)$ and $p_w(\theta)$, as defined by the Fourier series, are f_0 and x_0, respectively. Moreover, the flux through the system corresponding to the general pressure distribution $p(r,\theta)$ is simply $2\pi khc_0/\mu$. Combining these results it is seen at once that the production capacity of the well will be

$$Q=\frac{2\pi kh(\bar{p}_e-\bar{p}_w)}{\mu \log r_e/r_w}, \qquad (10)$$

showing that if $\bar{p}_e$, $\bar{p}_w$ are the averages of any arbitrary pressure distribution over the radii r_e, r_w, respectively, the total flow through the sand will be the same as if the average pressures were applied uniformly over their respective boundaries. The practical significance of this result will be obvious.

An analogous generalization of the formula obtained above for the case of strict radial symmetry refers to systems in which the true external boundary of the flow system is not strictly circular. One may then show that the production capacity may still be computed by a formula almost identical with that previously derived, namely,

$$Q=(2\pi kh\Delta p)/(\mu \log c/r_w), \qquad (11)$$

where Δp is the pressure differential between the external boundary (supposed at uniform pressure) and the well of radius r_w, and c is a constant depending on the shape of the external boundary, but which may be approximated by an appropriate estimate of the average of the distance of the external boundary from the well. Thus, in particular, for the circular boundary of radius r_e concentric with the well, $r=r_e$, as discussed above. For the case in which a circular boundary of radius r_e has its center at a distance δ from the well center it is found that $c=(r_e^2-\delta^2)/r_e$. In case the well is at a distance d from an infinite line source it may be shown that $c=2d$, and if the external boundary is a rectangle of sides $2a$, $2b$, with the well at its center, $c=4(ab)^{\frac{1}{2}}/\pi$. This general result is also evidently of considerable practical importance.

Systems where the compressibility of the liquid must be taken into account are either those of very large dimensions or such where the liquid has an abnormally high compressibility. The first class is involved, for example, in the treatment of the production of oil fields by virtue of extended water drives in which the field as a whole is lumped together so as to be equivalent to a single fluid sink. Since normal liquids have small compressibilities, of the order of 10^{-5}/atmos., the assumption of an abnormally high compressibility implies that the liquid has interspersed through it gas masses whose high elasticity gives the resultant system an effectively high compressibility. A very important case in which both of these conditions have been found to be fulfilled in practice is that of the production of oil from the so-called "East Texas" oil field, which is the largest thus far ever discovered. On the basis of a mechanism in which it is supposed that the oil of the field is being driven out by water encroaching into it from the adjacent water basin, of some 10,000 square miles in area, and that this water reservoir has dispersed through it with some degree of uniformity gas masses occupying 4 percent of the total pore volume of the reservoir, the detailed production history of this field over a period of 5 years has been predicted with an accuracy of better than 1 percent. As we cannot enter here into the mathematical details of the solution for this or similar problems involving the flow of compressible liquids, even though this analysis is merely based on an application of the well-known theory of the Fourier heat conduction equation, we shall simply state in quantitative form one minor result of interest. It is that the mass flux of a compressible liquid passing through any system under steady state conditions with an average density $\bar{\gamma}$ is the same as that if the liquid were incompressible but had the constant density $\bar{\gamma}$.

When the fluid is a gas and its state of motion varies with the time, general rigorous solutions can no longer be obtained in analytical form, since the fundamental partial differential Eq. (5) is nonlinear. For the steady state, however, the equation formally reduces to that of Laplace, and solutions can be obtained for all types of geometry which can be successfully treated by the well-known methods of potential theory. In fact the results obtained for the flow of incompressible liquids through sands can be taken over directly for the equivalent problem in the flow of gases by simply replacing the pressure differentials of the former by the difference between the $(1+m)$th powers of the pressures multiplied by $\gamma_0/1+m$. It will be recalled that m determines the thermodynamic character of the gas expansion according to the equation $\gamma=\gamma_0 p^m$. Thus, for example, the steady state flow of gas between two concentric circular boundaries of arbitrary pressure distributions can be immediately written down from the results already quoted for incompressible liquid systems as

$$Q=\frac{2\pi kh\gamma_0(\overline{p_e^{1+m}}-\overline{p_w^{1+m}})}{(1+m)\mu \log r_e/r_w}, \tag{12}$$

while that for noncircular external boundaries can be expressed as

$$Q=\frac{2\pi kh\gamma_0\Delta p^{1+m}}{(1+m)\mu \log c/r_w}. \tag{13}$$

Likewise the variation of the production capacity of a gas well with the penetration of the well into the producing horizon is exactly the same as that for a well producing a liquid. Moreover the properties of multiple well systems in which an array of wells are arranged in patterns or networks will be the same for both gas and liquid producing wells under steady state conditions.

As a whole the analysis of the subject of the flow of homogeneous fluids through porous media may be considered as fairly well completed although it is true that many specific problems have yet to be given explicit solutions. In particular, those in which gravity is the predominating driving agent and in which free surfaces exposed to the atmosphere are present, such as the seepage of water through dams or out of canals or ditches, have been brought into the fold of tractable problems only very recently. However, it is now possible by means of either graphical methods or the use of electrical models to determine the properties of almost any specific flow system that might be of practical interest. What remains is largely the application

of the necessary amount of numerical or manipulative effort in order to provide the answer to any particular question that the agricultural or civil engineer or the operators of gas fields may propose.

In a literal sense this is also the situation with respect to the extremely important phase of fluid flow through porous media in which heterogeneous fluids are involved, such as mixtures of gases and liquids. Such mixtures, in particular oil and natural gas, are, of course, those that are involved in the great majority of actual producing oil fields with which the petroleum engineer must deal. Within the last year the fundamental physical laws governing such flow systems have been established. The essential new and all important feature peculiar to such heterogeneous fluid systems is that the permeability coefficient k in Darcy's law is no longer an absolute and invariant constant of the medium which completely characterizes and defines the porous medium as the carrier of the fluid. For due to the pressure variations in the system dissolved gas will be continually evolved from the liquid as it flows towards regions of lower pressure. Moreover this gas will at the same time expand in volume. The result will obviously be the displacement of at least part of the liquid from the pores of the medium, and this too will increase as regions of lower pressure are approached. More specifically, it may be said that the volume composition of the mixture will vary from point to point within the flow system from a complete liquid saturation of the pores in those regions where the pressure exceeds the saturation pressure of the gas, to a distribution between the gas and liquid phases in which the space occupied by the gas phase may equal or even exceed that occupied by the liquid. Even if we focus our attention only upon the liquid flow it is clear that the permeability of the sand to the liquid, that is, the liquid flux per unit pressure gradient, will certainly decrease as more and more of the pore space is occupied by gas and less of it is available for the flow of the liquid as a continuous phase. And when we turn our attention to the gas phase it is obvious that the permeability to it as a free gas will increase as more of the pore space is occupied by free gas. Thus the permeability of the medium for the gas and liquid phases will not only differ from what they are when they are flowing individually in the sand, but moreover these two permeabilities will both vary with the local composition of the mixture, which may be defined by the local fractional pore space occupied by liquid and denoted as the liquid saturation. One must, therefore, generalize the concept of a porous medium whose conductivity of the fluids is independent of their nature, once their viscosities are taken into account, and must attribute to the porous medium a local structure defined by the local liquid saturation which in turn determines the permeabilities for the two fluid phases.

The basic problem of the empirical study of the flow of heterogeneous fluids through porous media is the determination of this relationship, namely, that between the permeabilities of the fluid phases and the saturation of the medium, which represents the volume composition of the mixture. This has recently been carried out by Wyckoff and Botset with an ingenious technique.[3] A typical set of results is shown in Fig. 3, obtained with a linear column of unconsolidated sand carrying water saturated with carbon dioxide. Of course, the details of these curves will vary with the character of the sand and the nature of the fluids, but the principal features are quite definite and unambiguous. These are:

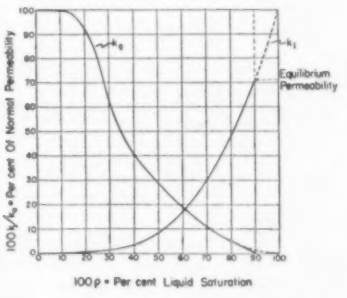

FIG. 3. Liquid (k_1) and gas $(k)_g$ permeabilities as a function of the liquid saturation, obtained with a 70–120 mesh sand carrying a water carbon dioxide mixture. Homogeneous fluid permeability $(k_0) = 17.8$ darcys. Dotted curves represent transient states of flow. Point marked "equilibrium permeability" gives maximal liquid saturation where steady state flow conditions can be maintained.

1. The sharp drop in the liquid permeability and the very slow rise of the gas permeability for small amounts of free gas dispersed through the sand.

2. The attainment of an almost complete

[3] R. D. Wyckoff and H. G. Botset, Physics **7**, 325 (1936).

homogeneous fluid permeability for the gas even with the presence of some 10–20 percent of liquid within the pores of the sand.

3. The peculiar property that for a given sand steady state conditions cannot be maintained until the gas saturation has built up to a certain minimal value, thus indicating an effective locking of the free gas in the pores before a flushing action of the gas develops to prevent further accumulation in the pores.

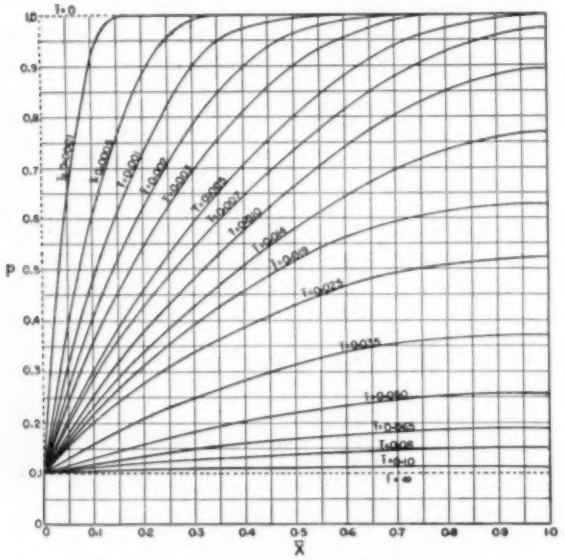

FIG. 4. History of the pressure (P) decline in a linear channel of sand filled with a liquid saturated with gas to a unit pressure, and having one terminal permanently closed and the other opened to production at the pressure 0.1. $\bar{t}$ is a dimensionless time after opening the system. $\bar{x}$ is the fractional distance from the open terminal.

Although a number of interesting conclusions can be drawn directly from these curves, detailed results can be obtained only from an analytical formulation and discussion of the problem. For this purpose one must set down Darcy's law in two separate equations, one for the liquid velocity and one for the velocity of the free gas, the coefficients of the pressure gradients being given by such curves as those of Fig. 3. Equations of continuity are then applied to express the conservation of the liquid mass flux and that of the gas, taking into account both the free gas and that dissolved in the liquid. Finally, the equations of state of the two fluid phases are introduced, that for the liquid being simply that it is effectively incompressible so that its density is constant, and that for the gas being Boyle's law or its equivalent, and Henry's law or an appropriate modification of it to take into account the solution of the gas in the liquid phase. The resulting two simultaneous partial differential equations in the two dependent variables, namely the fluid pressure and the liquid saturation, are then to be considered as governing the flow of any heterogeneous fluid system. Although the numerical constants and detailed form of the function representing the gas and liquid permeabilities will be dependent upon the nature of the sand and of the fluids, the form of these equations will remain the same for all porous media and fluid mixtures. And their solution for preassigned boundary and initial conditions for any specific problem can be discussed in exactly the same manner as for homogeneous fluid systems.

From a practical point of view it is just the feasibility of obtaining the desired solutions of these simultaneous partial differential equations which will determine the significance of the formulation. Unfortunately this question is a most embarrassing one, as the derivation of an analytic solution even if the empirical liquid and gas permeability curves are represented in analytic form seems a well nigh impossible task. In fact, the only hope whatever of deriving quantitative results seems to lie in attacking the problem numerically. Such numerical methods, however, are in general unsatisfactory because they require the numerical assignment of all the physical constants and a complete repetition of the solution when these constants are changed, and also because they inherently involve errors, the magnitudes of which are difficult to estimate precisely. One typical case has nevertheless been carried through in this manner.[4] It is that of a linear column of sand initially filled with liquid and saturated with gas to a uniform pressure, and which is then opened at one end where the pressure is lowered and maintained at a constant low value. Although the geometry of the system is very much simpler than those which one finds in practice, it does contain the essential physical features involved in the tapping of a virgin oil field and the tracing of its production history. The results

[4] M. Muskat and M. W. Meres, Physics **7**, 346 (1936).

of these calculations are shown in Figs. 4, 5, and 6. In Fig. 4 are shown successive stages in the depletion of the original pressure in the linear column. Its general nature is, of course, what is to be anticipated.

In Fig. 5 is shown a more interesting phase of the production history of this system, namely, the distribution of the liquid saturations along the length of the column. The general decline is, of course, to have been expected. But the significant feature, and what is of extreme importance from a practical point of view, is that the variation of the ultimate saturation distribution over the column is so limited The immediate implication is that almost as much of the liquid that is produced from a well is taken, per unit volume of the sand, at a large distance from it as in its immediate neighborhood. This result is contrary to the long established tradition in the oil industry to the effect that the recovery of oil decreases rapidly as one recedes from the sand face exposed by a well, so that unless neighboring wells are spaced closely much oil will be lost and remain permanently unrecovered when the pressure and original gas have been depleted. While the extrapolation of the results here obtained, which are based upon experiments with water and carbon dioxide flowing through unconsolidated sands, to actual oil field situations in which the sand is consolidated and the fluids are considerably different, may appear dangerous, the validity of the main features of the solution seems entirely reasonable.

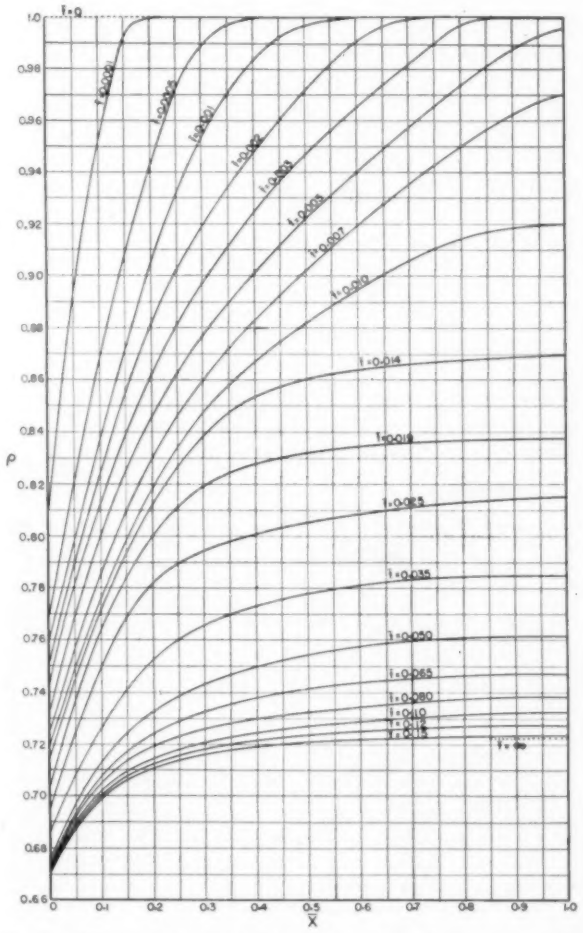

FIG. 5. History of the decline in the liquid content of the linear system of Fig. 4. $1-\rho$ = fractional depletion.

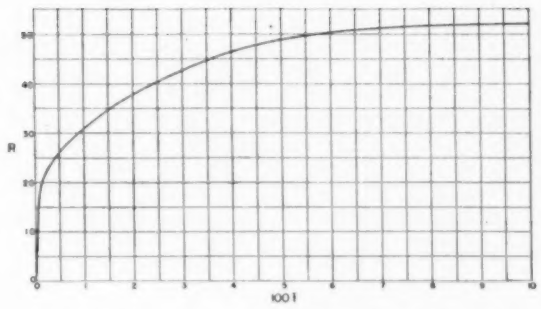

FIG. 6. Decline in the gas-liquid ratio (R = vol. of efflux gas at atmos. pressure per unit volume of liquid efflux) in the system of Fig. 4. Normal gas-liquid ratio of solution = 10.0.

The final result of interest is that of Fig. 6 in which is shown the variation of the gas-liquid ratio during the production history of the system. Here, too, a sound basis is provided for what has hitherto been intuitive judgment and uncorrelated observation that the gas liquid ratios of producing fields generally increase as the fields become depleted, thus implying a continually decreasing efficiency of the production.

To discuss further details and implications of the numerical results obtained from this particular example would carry one too far afield in the specialized subject of petroleum production. However, those mentioned should suffice to indicate not only the nature of the results that can be obtained by a physical study of heterogeneous fluid systems but also the underlying physical mechanism and processes that are involved. In fact it may be said that the basic physical principles involved in the flow of both

homogeneous and heterogeneous fluids through porous media are now definitely established. For the former there are available explicit solutions covering all types of specific problems of practical interest. And while for the latter the detailed solutions are very few in number, those that have been carried through definitely indicate that the manifold empirical field observations on gas-liquid mixture systems will find a satisfactory physical interpretation in terms of the elementary laws of flow deduced from laboratory experiments.

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Transformations Useful in Certain Antenna Calculations

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Transformation formulas are derived which greatly simplify computations relative to an antenna above a plane earth when the antenna is of a form easily specifiable in polar coordinates but not in cylindricals.

THERE exist formulae[1–3] which give simple looking expressions for the directional pattern of and total radiation from any antenna over any plane earth. These formulae use as a basis cylindrical coordinates with the z axis perpendicular to the ground. If the antenna is of a form easily describable in such cylindrical coordinates the various integrations necessary can often be done analytically and are not troublesome even if done numerically, and in such cases the formulae really are simple to handle. But there exist many antenna forms which do not fit in well with cylindrical coordinates and some of these are of practical importance. In such cases the numerical work would be possible but very tedious. However, a number of these antennas suggest the use of spherical polar coordinates and it is the purpose of the present paper to derive transformation formulae whereby the needed integrations can be done in spherical coordinates if that system is a convenient one.

The quantities it is desired to compute are the oscillator strengths f defined* by

$$f_{2,n}(\theta')=\frac{1}{2\pi k^2\sin^2\theta'}\int \mathbf{i}\cdot\mathbf{A}^*_{2,n}(\rho\phi z:\theta')d\tau, \quad (1)$$

$$f_{3,n}(\theta')=\frac{1}{2\pi k^2\sin^2\theta'}\int \mathbf{i}\cdot\mathbf{A}^*_{3,n}(\rho\phi z:\theta')d\tau,$$

where the $\mathbf{A}$ are vector functions of the cylindrical coordinates ρ, ϕ, z and of the parameter θ'. They are defined as follows. Let

$$\xi_n(\rho\phi z:\theta')=e^{i(kz\cos\theta'+n\phi)}J_n(k\rho\sin\theta') \quad (2)$$

and then

$$\begin{aligned}\mathbf{A}_{2n}&=\nabla\times\mathbf{k}_z\xi_n=(1/k)\nabla\times\mathbf{A}_{3n},\\ \mathbf{A}_{3n}&=(1/k)\nabla\times\mathbf{A}_{2n}.\end{aligned} \quad (3)$$

If the quantities f of (1) are to be computed and the current distribution is in spherical polar coordinates it is plain that we must get expressions for the $\mathbf{A}$ in spherical coordinates. Since the cylindrical $\mathbf{A}$ are solutions of the vector wave equation we can build any $\mathbf{A}(\rho\phi z:\theta')$ up of solutions of the vector wave equation in any other coordinates, for example sphericals. Convenient solutions of the vector wave equation in spherical coordinates are known[4] and will be denoted by[5] $\mathbf{A}_{2,ln}(r\theta\phi)$, $\mathbf{A}_{3,ln}(r\theta\phi)$. Thus we may write

[1] W. W. Hansen and J. G. Beckerley, Physics **7**, 220 (1936).
[2] W. W. Hansen and J. G. Beckerley, Proc. I.R.E. **24**, 1594 (1936).
[3] W. W. Hansen, Physics **7**, 460 (1936).
* The notation $\mathbf{A}^*$ is used to denote the complex conjugate of $\mathbf{A}$.

[4] G. Mie, Ann. d. Physik **25**, 377 (1908); Bateman, "Electrical and Optical Wave Motion," *Handbuch der Physik*, M. Born, *Optik*, W. W. Hansen, Phys. Rev. **47**, 139 (1935). The notation here used is that of the last paper cited. See also reference 2, where explicit expressions are given for these functions.
[5] The possibility that the coefficients should be $b_{ln'}$ and should have a summation over both l and n' is easily dismissed by reasons of symmetry since the two coordinates ϕ are the same.

$$\mathbf{A}_{2,n}(\rho\phi z : \theta') = \sum_l (b_{2ln}(\theta')\mathbf{A}_{2ln}(r\theta\phi) + b_{3ln}(\theta')\mathbf{A}_{3ln}(r\theta\phi)) \quad (4)$$

and a similar expression for $\mathbf{A}_{3n}$. Then the problem is to determine the expansion coefficients b.

To determine the coefficients we multiply both sides of the equation by a particular $\mathbf{A}_s(r\theta\phi)$ and integrate throughout a large sphere whereupon, because of the orthogonality of the $\mathbf{A}_s$, all but one of the terms on the right disappear and we have an expression for one of the b in terms of integral of $\mathbf{A}_{2,n}(\rho\phi z : \theta') \cdot \mathbf{A}_s(r\theta\phi)$. It is the evaluation of this integral that causes trouble and this for two reasons: first, the integrand is written as a function of both ρ, ϕ, z and r, θ, ϕ, and second, a scalar product must be taken with one vector given in cylindrical components and the other in spherical coordinate components.

We avoid these difficulties by two devices. For one we find the Cartesian components of both the vector functions so that the dot product is easily handled. We find the Cartesian components because in this system alone each component of a solution of the vector wave equation is a solution of the scalar wave equation: for example the Cartesian components of $\mathbf{A}_{2,n}$ are expressible as combinations of ξ_n. For the other we find means of expressing the $\xi_n(\rho\phi z : \theta')$ occurring in the definition of $\mathbf{A}_{2,n}(\rho\phi z : \theta')$ in terms of the $\xi(r\theta\phi)$ involved in $\mathbf{A}(r\theta\phi)$. The integration is then performed without particular difficulty but with liberal use of orthogonality relations between spherical harmonics and the various recursion formulae connecting these functions.

The actual computation proceeds as follows. By methods previously explained[1, 4] we find the Cartesian components, the results being as follows:

$$\mathbf{A}_{2,n}(r\phi z : \theta') = \mathbf{k}_x \frac{i \sin\theta'}{2}(\xi_{n+1} + \xi_{n-1}) + \mathbf{k}_y \frac{\sin\theta'}{2}(\xi_{n+1} - \xi_{n-1}),$$
$$\mathbf{A}_{3,n}(r\phi z : \theta') = \mathbf{k}_x \frac{-i \sin\theta' \cos\theta'}{2}(\xi_{n+1} - \xi_{n-1}) + \mathbf{k}_y \frac{-\sin\theta' \cos\theta'}{2}(\xi_{n+1} + \xi_{n-1}) + \mathbf{k}_z \sin^2\theta' \xi_n \quad (5)$$

for the cylindrical $\mathbf{A}$. And for the spherical $\mathbf{A}$ we find

$$\mathbf{A}_{2ln}(r, \theta, \phi) = \mathbf{k}_x \frac{i}{2}((l-|n|)(l+|n|))^{\frac{1}{2}}\xi_{l,n+1} + ((l-|n|+1)(l+|n|))^{\frac{1}{2}}\xi_{l,n-1}$$
$$+ \mathbf{k}_y \tfrac{1}{2}((l-|n|)(l+|n|))^{\frac{1}{2}}\xi_{l,n+1} - ((l-|n|+1)(l+|n|))^{\frac{1}{2}}\xi_{l,n-1} - \mathbf{k}_z\, i\, n\, \xi_{l,n},$$

$$\mathbf{A}_{3ln} = \mathbf{k}_x \frac{-1}{2}\left[\left(\frac{l(l+2)(l+|n|+1)(l+|n|+2)}{(2l+1)(2l+3)}\right)^{\frac{1}{2}}\xi_{l+1,n+1} - \left(\frac{l(l+2)(l-|n|+1)(l-|n|+2)}{(2l+1)(2l+3)}\right)^{\frac{1}{2}}\xi_{l+1,n-1}\right.$$
$$\left. - \left(\frac{(l-1)(l+1)(l-|n|)(l-|n|-1)}{(2l-1)(2l+1)}\right)^{\frac{1}{2}}\xi_{l-1,n+1} + \left(\frac{(l-1)(l+1)(l+|n|)(l+|n|-1)}{(2l-1)(2l+1)}\right)^{\frac{1}{2}}\xi_{l-1,n-1}\right]$$
$$+ \mathbf{k}_y \frac{i}{2}\left[+\left(\frac{l(l+2)(l+|n|+1)(l+|n|+2)}{(2l+1)(2l+3)}\right)^{\frac{1}{2}}\xi_{l+1,n+1} + \left(\frac{l(l+2)(l-|n|+1)(l-|n|+2)}{(2l+1)(2l+3)}\right)^{\frac{1}{2}}\xi_{l+1,n-1}\right. \quad (6)$$
$$\left. - \left(\frac{(l-1)(l+1)(l-|n|)(l-|n|-1)}{(2l-1)(2l+1)}\right)^{\frac{1}{2}}\xi_{l-1,n+1} - \left(\frac{(l-1)(l+1)(l+|n|)(l+|n|-1)}{(2l-1)(2l+1)}\right)^{\frac{1}{2}}\xi_{l-1,n-1}\right]$$
$$- \mathbf{k}_z\left(\left[\frac{l(l+2)(l+|n|+1)(l-|n|+1)}{(2l+1)(2l+3)}\right)^{\frac{1}{2}}\xi_{l+1,n} + \left(\frac{(l-1)(l+1)(l+|n|)(l-|n|)}{(2l-1)(2l+1)}\right)^{\frac{1}{2}}\xi_{l-1,n}\right].$$

We could now perform the integration if we had an expression for the cylindrical coordinate wave function $\xi_n(\rho\phi z : \theta')$ in terms of spherical coordinate wave functions $\xi_{l,n}(r\theta\phi)$. This we find by

considering both wave functions as built up of plane waves with amplitudes weighted in the proper way as a function of the direction of the plane waves.[6] The desired expression is then easily found by comparing the weight functions.

Thus we express the cylindrical wave function as a sum of plane waves.

$$\xi_n(\rho\phi z : \theta') = \frac{1}{2\pi i^n}\int_{-\pi}^{+\pi}\int_0^{\pi} e^{ikX}e^{in\phi'}\frac{\delta(\theta'-\theta'')}{\sin\theta'}\sin\theta''d\theta''d\phi', \tag{7}$$

where

$$X = z\cos\theta' + x\sin\theta'\cos\phi' + y\sin\theta'\sin\phi' \tag{7a}$$

and $\delta(x)$ is a function that is zero when $x\neq 0$ and is infinite at $x=0$ in such a way that the integral of $\delta(x)dx$ is unity.

The spherical wave functions are also easily expressed in terms of plane waves

$$\xi_{l,n}(r\theta\phi) = \left(\frac{(2l+1)(l-|n|)!}{8l(l+1)(l+|n|)!}\right)^{\frac{1}{2}}\frac{1}{(2\pi)^{\frac{1}{2}}}\frac{1}{i^n}\int_{-\pi}^{+\pi}\int_0^{\pi} e^{ikX}P_l^{|n|}(\theta')e^{in\phi'}\sin\theta'd\theta'd\phi'. \tag{8}$$

Comparing (7) and (8) we see that the desired result may be achieved by expanding $\delta(\theta'-\theta'')/\sin\theta'$ in a series of spherical harmonics. The expansion is immediately written down as

$$\frac{\delta(\theta'-\theta'')}{\sin\theta'} = \sum_l \frac{(2l+1)(l-|n|)!}{2(l+|n|)!}P_l^{|n|}(\theta')P_l^{|n|}(\theta''). \tag{9}$$

This is now inserted in (7) the $P_l^n(\theta')$ taken outside the integral and the integration done by using (8). The result is[7]

$$\xi_n(\rho\phi z : \theta') = 2\sqrt{\pi}\sum_l\left(\frac{l(l+1)(2l+1)(l-|n|)!}{(l+|n|)!}\right)^{\frac{1}{2}}P_l^{|n|}(\theta')\xi_{l,n}(r\theta\phi). \tag{10}$$

The integrations are now easily done, orthogonality relations greatly simplifying matters by causing most of the terms of (4) to drop out in any particular integration. After considerable reduction,[8] it is found that the desired results can be written in rather simple form.

$$\begin{aligned}\mathbf{A}_{2,n}(\rho\phi z : \theta') = 2\sqrt{\pi}\sin\theta'\sum_l\left(\frac{(2l+1)(l-|n|)!}{l(l+1)(l+|n|)!}\right)^{\frac{1}{2}}i^{l-n+1}\\ \times\left(\frac{d}{d\theta'}P_l^{|n|}(\theta')\mathbf{A}_{2ln}(r\theta\phi) - \frac{n}{\sin\theta'}P_l^{|n|}(\theta')\mathbf{A}_{3ln}(r\theta\phi)\right),\\ \mathbf{A}_{3,n}(\rho\phi z : \theta') = 2\sqrt{\pi}\sin\theta'\sum_l\left(\frac{(2l+1)(l-|n|)!}{l(l+1)(l+|n|)!}\right)i^{l-n+1}\\ \times\left(\frac{n}{\sin\theta'}P_l^{|n|}(\theta')\mathbf{A}_{2ln}(r\theta\phi) - \frac{d}{d\theta'}P_l^{|n|}(\theta')\mathbf{A}_{3ln}(r\theta\phi)\right).\end{aligned} \tag{11}$$

It is to be noted that the functions of θ' occurring on the right are exactly the same as the functions of θ appearing in the θ and ϕ components of $\mathbf{A}_{2ln}$ and $\mathbf{A}_{3ln}$. These have been tabulated in reference (2). From this result the f are easily calculated by integrating $\mathbf{i}\cdot\mathbf{A}^*(r\theta\phi)d\tau$, and summing. A symbol has been defined[2, 4] for these integrals

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[6] See Whittaker and Watson, *Modern Analysis*, fourth edition, Par. 18.6 and ff. The author is greatly indebted in this connection, to Professor P. M. Morse of M.I.T. who pointed out to him this powerful method of Whittaker's and explained many illuminating examples not to be found in the literature.

[7] The author is aware that the expansion here found (Eq. (10)) is a special case of an equation in Watson's *Bessel Functions*, Par. 11.5, Eq. (9). However, it is felt that the proof given here if not as rigorous will perhaps be more interesting and suggestive to physicists.

[8] See Appendix I for a collection of formulas useful for making these reductions and in other similar work.

$$a_s = \int \mathbf{i} \cdot \mathbf{A}^*_s(r\theta\phi)\, d\tau \tag{12}$$

and using this notation we may write

$$\begin{aligned} f_{2n}(\theta') &= \frac{1}{\sqrt{\pi k^2 \sin\theta'}} \sum_l \left(\frac{(2l+1)(l-|n|)!}{l(l+1)(l+|n|)!} \right)^{\frac{1}{2}} i^{n-l-1} \left(\frac{d}{d\theta} P_l^{|n|}(\theta') a_{2ln} - \frac{n}{\sin\theta'} P_l^{|n|}(\theta') a_{3ln} \right), \\ f_{3n}(\theta') &= \frac{1}{\sqrt{\pi k^2 \sin\theta'}} \sum_l \left(\frac{(2l+1)(l-|n|)!}{l(l+1)(l+|n|)!} \right)^{\frac{1}{2}} i^{n-l-1} \left(\frac{n}{\sin\theta'} P_l^{|n|}(\theta') a_{2ln} - \frac{d}{d\theta'} P_l^{|n|}(\theta') a_{3ln} \right). \end{aligned} \tag{13}$$

We can understand why the appearance of angle factors like those of the spherical **A** is inevitable and get a good check of the result (13) by considering a special case. Thus suppose we have a current distribution such that some particular a_s, say a_{2ln} is finite while all other a_s are zero. Then there are two ways of computing the field at large distances and of course both should give the same result. For one method we can use formula (8), reference 4 (repeated as formula (4), reference 2) which says that the field is

$$\mathbf{E} = -(1/c) a_{2ln} \mathbf{A}'_{2ln}(r\theta\phi). \tag{14}$$

Then we use expressions given in reference 2 (Eq. (8)) to get an approximation for $\mathbf{A}'$ valid at large distances. Even without looking this up, however, we can be sure that **E** will have an angle dependence like that of $\mathbf{A}_{2ln}$. In fact we find

$$\mathbf{E} \leqq a_{2ln} \frac{k}{c} \left(\frac{(2l+1)(l-|n|)!}{8l(l+1)(l+|n|)!} \right)^{\frac{1}{2}} \left(\frac{2}{\pi} \right)^{\frac{1}{2}} i^{-l-1} \frac{e^{ikr}}{kr} e^{in\phi} \left(-\mathbf{k}_\theta \frac{in}{\sin\theta} P_l^{|n|}(\theta) + \mathbf{k}_\phi \frac{d}{d\theta} P_l^{|n|}(\theta) \right), \quad kr \gg l^2. \tag{15}$$

This would be the normal and direct way of finding **E** at large distances. But we should be able to get the same result as follows. First we use the transformation formula (13) to compute the oscillator strengths f in cylindrical coordinates. Then we use formula (12), reference 3, which gives **E** at large distances in polar coordinates in terms of the f. As there is only one a_s there will be no summation and only two f will occur, f_{2n}, and f_{3n}, so the computation is child's play. Using (13) we find that as there is no a_{3ln} and no summation

$$f_{2n} = \frac{1}{\sqrt{\pi k^2 \sin\theta'}} \left(\frac{(2l+1)(l-|n|)!}{l(l+1)(l+|n|)!} \right)^{\frac{1}{2}} i^{n-l-1} \frac{d}{d\theta'} P_l^{|n|}(\theta'). \tag{16}$$

The expression for f_{3n} is not written. Now Eq. (12), reference 3 says that at large distances the ϕ component of **E** is obtained by replacing θ' in f_{2n} by θ and multiplying by $\sin\theta$ and various constants. Plainly if we do this (16) will give the expected result (15) provided the constants work out correctly as in fact they do. Moreover the omitted f_3 gives the correct θ component. Thus we understand the appearance in (11) and (13) of angle factors identical with those previously encountered in connection with the spherical **A**. In fact one could derive (11) by considerations like the above and so avoid the tedious algebra of the omitted reductions that lie between Eqs. (10) and (11).

As a more practical problem illustrative of the use of the results of this paper, consider the ordinary tilted wire type of antenna. For definiteness take one a single wave-length long with a corresponding tilt angle of 30° as illustrated in Fig. 1. Plainly exact computation in cylindrical coordinates would be difficult[9] whereas if one puts the origin of a polar coordinate system anywhere on the wire the a_s are easily found; in fact, closed formulas for the integrals occurring are given in reference 2. To use the present results in a perfectly straightforward way one would put the origin of the spherical coordinate system at the grounded end of the

[9] It seems likely that the antenna in question can be well approximated by two dipoles at the current loops. If this approximation is satisfactory direct calculation in cylindrical coordinates can easily be done.

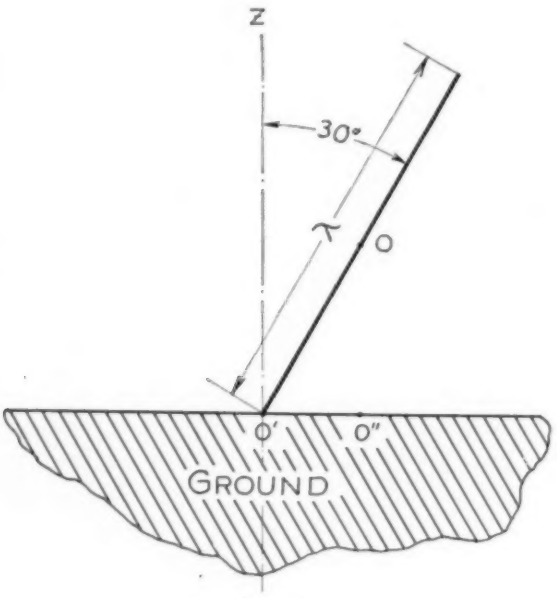

FIG. 1.

wire (O' in Fig. 1) and proceed. However, if we put the origin at the center of the wire (O in Fig. 1) the number of nonvanishing a_s will be greatly reduced and this for two reasons: first, symmetry will in this case cause half the a_s to be identically zero, and second, the antenna only extends half as far from the origin and this will cut the highest important value of l by roughly one-half and reduce the total number of a_s occurring by a still larger factor.[10] The f computed from these a_s by (13) will of course correspond to having $z=0$ at O instead of at the ground, but, as we shall see, this is easily changed by multiplying the f by a phase factor.

Putting the origin at O then, there are only two groups of a_s of important size, $a_{3,2,n}$ and $a_{3,4,n}$. In reference 2 will be found tables which enable one to write down these a_s immediately. The various f, of which there are nine, are then computed using (13). As there are only two values of l the computations for $f_{34}, f_{31}, f_{32}, f_{21}, f_{22}$ reduce to the addition of two trigonometric functions (the P_l^n) with weight factors depending on the a_{32n} and a_{34n}. In the expressions for the f with n values of 3 and 4 only one term occurs in the summation. Thus the f are easily computed.

In this way we find the values the f would have if the origin were taken at O. But if we are to take the ground into account we must put the origin at the surface of the ground, for example at O'' and it remains to find the values of f corresponding to this choice of origin. It is easily verified, however, by a simple linear transformation, that the entire effect of moving the origin from O to O'' is to multiply all the f by e^{-imz_0} with z_0 the distance from O to O'', i.e., $\lambda/2 \cos 30°$. Thus we have only to multiply the f computed above by exp. $(-i\pi\sqrt{3}/2 \cos\theta')$. But this has modulus one so its effect may be taken in by rotating the vectors representing f in the complex plane by an angle $\pi\sqrt{3}/2 \cos\theta'$. Once the f are found in this way the directional pattern is known by (12) reference 3 and the radiation resistance is computed by integrating the f as directed by (15), reference 2, and so we can consider the problem solved.

However, we do not plan to erect such an antenna in the near future so the numbers to be obtained by twelve hours or so of computation have no special interest to us. For this reason we have not actually completed the calculations described above. We have, however, done enough representative sections of them to make sure that their complete performance, though somewhat tedious because of the bookkeeping involved in keeping track of nine f, etc. is actually possible as represented above and this in a noninfinite time. We believe that this is more than can be said of any other method of calculation which takes the ground into account and does not use approximations.

APPENDIX I

Anyone wishing to check the present analysis or do work along the same lines will find the following formulas useful.

$$\sin\theta P_l^n = \frac{1}{2l+1}(P_{l+1}^{n+1} - P_{l-1}^{n+1})$$

$$= \frac{1}{2l+1}((l+n)(l+n-1)P_{l-1}^{n-1} - (l-n+2)(l-n+1)P_{l+1}^{n-1}),$$

$$\cos\theta P_l^n = \frac{1}{2l+1}((l+n)P^n{}_{l-1} + (l-n+1)P^n{}_{l+1}),$$

$$\frac{d}{d\theta}P_l^n = \tfrac{1}{2}((l-n+1)(l+n)P_l^{n-1} - P_l^{n+1}),$$

$$\frac{n}{\sin\theta}P_l^n = \tfrac{1}{2}\cos\theta((l-n+1)(l+n)P_l^{n-1} + P_l^{n+1}) + n\sin\theta P_l^n.$$

If desirable the last formula can be further expanded by the use of the first two.

[10] See reference 2, page 1612.

The Application of Paschen's Law to the Re-Ignition of an Arc

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(Received December 21, 1936)

An a.c. arc, in order to restrike after passing through current zero, requires a potential considerably higher than the normal burning potential. This re-ignition potential is investigated for short gaps in nitrogen, using pure graphite electrodes with spacings up to two mm and pressures up to 500 cm Hg. The re-ignition potential is found to have two characteristics. One of these characteristics is followed for the arcs in which the cathode spot is maintained by field emission, and the other is followed for the "thermionic" arc. Relations are obtained between this re-ignition potential and both the gas pressure and the gap spacing, with the arc current as parameter. These relations may then be combined into a single relation between the reignition potential and the product of the pressure and spacing. This gives a function that is of the same form as the Paschen law for the initial sparking potential of a gap. The constants of this function are dependent on the arc current, the gas in the space, and the constants of the circuit. That the constants of the re-ignition function are not the same as those for the sparking potential law is to be expected from the very dissimilar conditions applying in the space. Extreme purity of electrode materials and of gas, as well as extreme care in obtaining the experimental results, are essential.

Introduction

IN 1889 Paschen[1] formulated the law stating that the spark potential (breakdown voltage) of a gap could be expressed as a function of the product of the pressure of the gas in the space and the separation of the electrodes. This law has been verified and extended by later investigators to higher and to lower pressures. The experimental work of Thoma[2] and Heer[2, 3] proves that this law may be extended to both the ignition and the burning potential of the glow discharge over a range of pressures from 6 mm of mercury to atmospheric. Thomson[4] found that this relation also applied for glow discharges at high frequencies. Wheatcroft[5, 6] and Barker[5] arrive at essentially the same conclusions from their experiments at low pressures. Research previously reported[7, 8] indicated that a relation similar to Paschen's law might also apply to the re-ignition potential of an a.c. arc; that is, the voltage that must be reached after the current has passed through zero before the arc is re-established in the opposite direction.

The conditions in the case of re-ignition of a self-sustained discharge by an alternating potential are vastly unlike those existing in the case of the original breakdown of the gap. First, the number of free ions, both positive and negative ions and electrons, is very much larger than in the fresh gas; second, after one-half cycle of arcing, the gas temperature will be considerably higher than initially; third, the active portion of the electrodes will have become heated, the extent of this heating dependent on the current of the discharge; fourth, under certain conditions considerable electrode material will be vaporized into the gap region. Notwithstanding these differences, the importance of which depends upon the geometry of the gap, the magnitude of the previous current, and the time available to the discharge space for reassuming normal conditions, the earlier work at low pressures by one of the authors[8] demonstrated that there did exist a relation between this re-ignition potential and the pressure of the gas in the gap, that bore remarkable similarity to the relations obtained by Paschen for the initial sparking potential of the gap. Research carried out recently at the Harvard Graduate School of Engineering has been made with the object of verifying this relation for high pressures. The results presented in this paper include this extension of the relation between arc re-ignition potential and pressure, and also add to the evidence that the re-ignition

[1] Paschen, Wied. Ann. **37**, 69 (1889).
[2] H. Thoma and L. Heer, Zeits. f. tech. Physik **14**, 385 (1933).
[3] L. Heer, Arch. f. Elekt. **27**, 196 (1933).
[4] J. Thomson, Phil. Mag. **18**, 696 (1934).
[5] E. L. E. Wheatcroft, H. Barker, Phil. Mag. **20**, 562 (1935).
[6] E. L. E. Wheatcroft, Phil. Mag. **20**, 578 (1935).
[7] S. S. Mackeown, J. D. Cobine, F. W. Bowden, Elect. Eng. **53**, 1081 (1934).
[8] J. D. Cobine, Physics **7**, 137 (1936).

potential of an arc for given current and gas is a function of the product of gap separation and gas pressure only.

Apparatus and Methods

A pressure chamber was designed and constructed to hold exchangeable electrodes in any gas up to pressures of about 10 atmospheres; permitting pressure measurements with an accuracy of 1 percent, and gap measurements to an absolute accuracy of 0.005 mm. Commercial nitrogen, treated by passing the gas over hot copper and through calcium chloride, was used in the tests herein reported. The tests were made by supplying the arc with power from a 15-kva, 10-kv, 60-cycle transformer through a current limiting resistance on the arc side of the transformer. The current for each point was taken with an iron vane ammeter, and the voltage with a carefully adjusted and calibrated cathode-ray oscillograph. It is important that the latter instrument be calibrated each time that it is used, in order to eliminate errors due to supply voltage change, variation of the ambient electrostatic and electromagnetic fields, and other sources of long-time shift in beam deflections. The utmost care was taken to maintain the purity of the spectrographic carbons used as electrodes and also in adjusting and reading the instruments, thus reducing errors to a minimum and making possible the duplication of any of the values. The diameter of the electrodes was 6.4 mm. The maximum spacing that could be employed with these electrodes was about 2 mm, beyond which the ratio of spacing to diameter was so large that edge effects assumed considerable importance. It is important to note that for duplication of these results, it is essential to duplicate the equipment, potential supply, and the gas and electrode purity. It has been found in this research, as indicated by other authors in dealing with Paschen's law for the sparking potential, that factors such as circuit impedance, rate of voltage rise, gradient in the space, etc., are most important in interpretation and reproduction of results. Thus the important significance of these results is not in the specific values of the reignition potential for any given combination of pressure, gap length, and current, but in the trends of the curves, which should be obtainable with any similar equipment and voltage.

Results

The curves of Fig. 1 show the relation between the re-ignition potential of the gap and the pressure of the gas in the space for different values of arc current. The uppermost curve is the spark breakdown function for the 1 mm gap, which follows the Paschen law. Two different types of reignition characteristics are shown. The one for currents below *2.5* amperes is definitely that of a field emission arc, as is evidenced by the

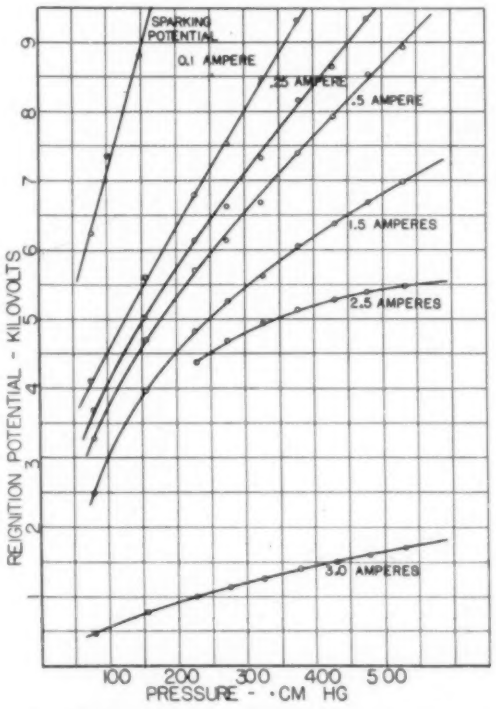

Fig. 1. Arc re-ignition potential as a function of gas pressure for a 1 mm gap in N_2. Parameter is the r.m.s. arc current.

rapid motion of the arc over the electrode surface. The other type of re-ignition characteristic is for currents above 2.5 amperes and represents the relation existing for a thermionic emission arc. The arc for these larger currents is relatively fixed in position and has the other characteristics of this type of arc. The sparking potential curve is the theoretical limit for the reignition curves as the current of the self-sustained discharge approaches zero. For Fig. 1, the gap was adjusted to one millimeter which,

as the later curves show, is an optimum setting for the electrodes employed. The curves show that the re-ignition potential is a definite, continuous, increasing function of the pressure from atmospheric to 500 cm of mercury absolute. The constants of the function representing this re-ignition relation are obviously not the same as those for the sparking potential, but the function is just as definite, and quite as smooth. Because of the relatively high value of the lowest pressure used, the minimum voltage of a typical Paschen law curve was not reached. This minimum was closely approached in the early low pressure work.[8]

Fig. 2 shows the relation obtained between the reignition potential and the gap separation at atmospheric pressure for several values of the current. As in Fig. 1, there is evident a smooth, definite variation with the length of the gap of the potential necessary to restrike the arc. As in Fig. 1, the upper curve is the zero current, or sparking potential curve for the gap and pressure employed.

Leading to the final presentation of the form of Paschen's law applying to arc re-ignition

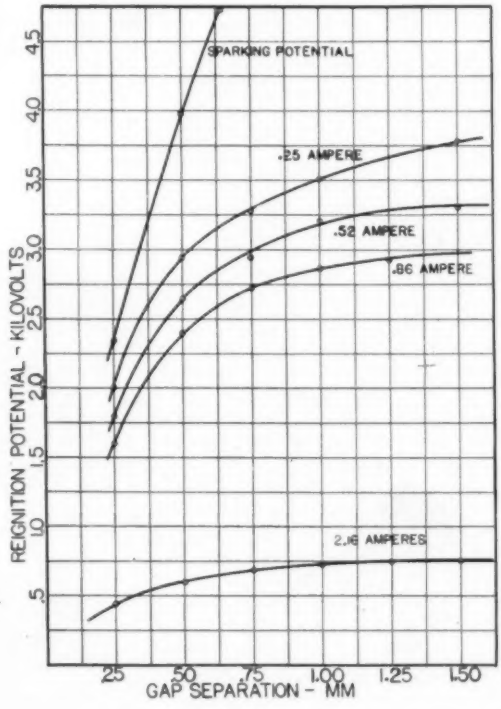

FIG. 2. Arc re-ignition potential as a function of gap length for N_2 at 77 cm Hg. Parameter is r.m.s. arc current.

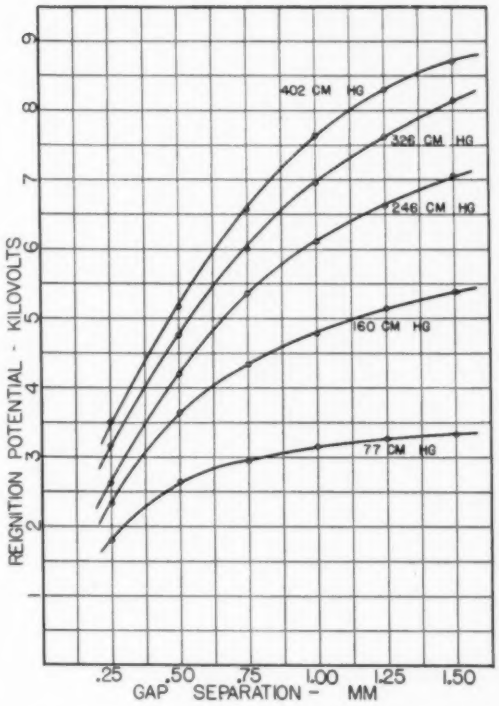

FIG. 3. Arc re-ignition potential as a function of gap length for an r.m.s. current of 0.525 ampere in N_2. Parameter is gas pressure in cm Hg.

potentials, Fig. 3 shows the variation of the reignition potential with gap length for several pressures at constant current. In order to make the test conclusive, a large number of points were determined for a current of 0.525 amp., as indicated by the curve in Fig. 4. As this curve was seen to be regular for this value of current, the other curve was drawn from typical key-point values. As is to be expected from Figs. 1 and 2, the relations of Fig. 3 are of the same type, and are quite regular.

Fig. 4 shows the re-ignition potential of the arc plotted as a function of the product of the pressure and the gap length for constant current. This relation is similar to that previously obtained by many investigators for the sparking potential of a gap. For the re-ignition potential, the function is determined in part by the current during the half-cycle previous to re-ignition, thus making the current a parameter. Actually, there is another parameter implied in addition to the arc current and the gas, namely, the nature of the voltage source. The fact that the experimental results lie very closely on the curve for 0.525 amp., Fig. 4, indicates the existence of a

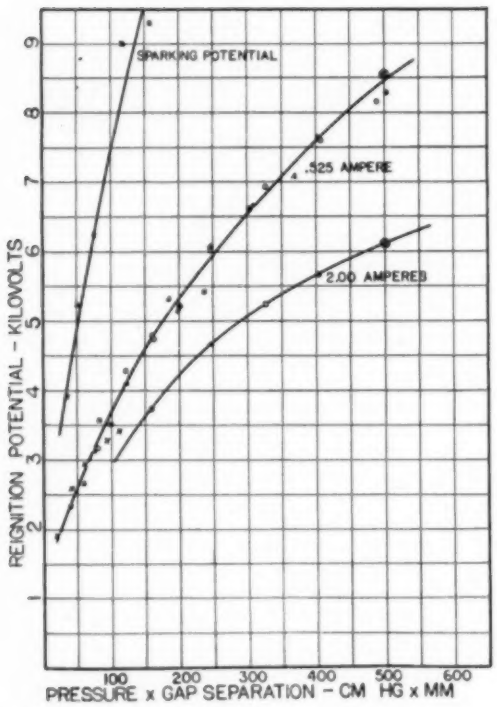

FIG. 4. Paschen's law for arc re-ignition potential in N_2. Parameter is r.m.s. arc current. Double circle, gas pressure = 500 cm Hg; dot, gas pressure = 403 cm Hg; single circle, gas pressure = 326 cm Hg; triangle, gas pressure = 246 cm Hg; square, gas pressure = 160 cm Hg; cross, gas pressure = 77 cm Hg.

definite relation between the restriking potential of a gap and the product of the gas pressure and gap separation.

DISCUSSION

The results of this research, as shown by the diagrams, substantiate the conclusion that the reignition potential of an arc is related to the pressure of the gas and the gap length by a function similar in form to that for the original phenomenon of striking the arc as a spark breakdown. The function for the re-ignition potential will obviously have different constants from those obtained for the initial sparking potential, because the conditions existing in the gap space for spark breakdown and for arc reignition are very different. This difference of conditions requires additional parameters for the complete determination of the arc reignition potential. The characteristics are determined by all factors affecting the degree of ionization of the gas at the instant of zero current and the rate of change of that ionization. The degree of ionization at zero current is a direct function of the arc current. In the absence of a reappearing voltage, the ionization when the current is low will quickly disappear by recombination in the gas and neutralization at the electrode surfaces. For higher values of the current, the volume deionization will be slower, because in the presence of thermal ionization, deionization will proceed at a much slower rate, determined by a time constant characteristic of the gas. Obviously, in the case of small current arcs, the reapplied voltage must be very much higher or must be applied at a much higher rate than for heavy currents if deionization is to be arrested. This is seen to be the case with the experimental results shown in Figs. 1 to 4. It is believed[7] that the re-ignition of the field emission arc consists in the establishment of a kind of glow discharge by the reapplied voltage. This discharge becomes unstable at the reignition point due to the cumulative effects of positive ion bombardment, increased field at the cathode due to positive ion space charge, effects of metastable atoms, etc. All these factors increase electronic emission at the cathode, and in consequence an arc cathode spot is developed. The similarity of the re-ignition functions for the arc and the glow discharge, coupled with the fact that the glow discharge is known to exist at atmospheric pressures,[2, 3, 9, 10] indicates that this theory is rational.

Although results for nitrogen only are given, the conclusions apply equally to air and oxygen, whose characteristics have been found to exist in the same general form.

Invaluable advice and assistance in the research and in preparation of this paper were generously given by Professors E. L. Chaffee, H. E. Clifford and C. L. Dawes of the Graduate School of Engineering.

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Rheological Properties of Asphalts IV*

Observations Concerning the Anomalous Flow Characteristics of Air-Blown Asphalts†

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A great many of the asphaltic bitumens used commercially possess anomalous flow properties to some degree. Although all asphalts are probably elastic in some measure, detection and measurement of this property are difficult in the cases of certain bitumens, especially soft ones where the permanent deformation obscures the elastic effects. Data obtained by means of the rotating cylinder type of viscometer at a low shearing stress show the presence in an asphalt of elastic fore- and after-effects. Frequently, when an asphalt is subjected to increasing shearing forces, a "threshold" value is reached above which the "viscosity" at a particular stress decreases with time until a constant value is obtained. If an asphalt is subjected to a high shearing stress (above the "threshold" value) in a rotating cylinder viscometer and the stress is reduced suddenly to a low value, the viscosity will increase gradually even though the asphalt is being worked constantly. Another manifestation of thixotropy is the age-hardening of asphalts. This increase of viscosity with time, which varies greatly with different asphalts, can be overcome by heating or mechanical working. Upon standing, the viscosity again increases with time. Also, it has been found that for many asphalts the "viscosity" diminishes with increased shearing stress. The extent of these anomalous flow characteristics is dependent upon the source of material, the method and extent of processing to which it is subjected, and the temperature and rate of shear at which the measurements are made. Using numerous kinds and consistencies of asphalt, correlations of the Bingham-Stephens alternating stress, the falling coaxial cylinder, and the conicylindrical rotation viscometers have been made. Comparisons were made at essentially the same mean shearing stresses in all three instruments for a particular asphalt. Good agreement was found when the asphalts were essentially viscous. Deviations of the results obtained for the three instruments became greater as the anomalous flow properties became more pronounced.

IT is generally agreed among those who have studied the rheological nature of bituminous materials that certain asphalts behave essentially as viscous liquids at normal atmospheric temperatures. On the other hand, many asphalts used commercially possess to varying extents certain anomalous flow characteristics frequently displayed by colloidal systems. Recently the authors showed[1] that the existence and magnitude of these anomalous flow properties depend not only on the type of bitumen, but also on the temperature and rates of shear at which measurements are made, and on the method and degree of processing to which the asphalt has been subjected. Bituminous technologists know that the nature of flow in air-blown asphalts is more complex than in most steam or vacuum-refined asphalts. In the present paper elasticity, thixotropy and non-Newtonian flow will be discussed with reference to their occurrence in air-blown asphalts; in addition, some mention will be made of the effects that anomalous flow properties have on the results obtained by different types of viscometers.

Elasticity

Undoubtedly all asphalts are elastic in some measure, but the detection and evaluation of this property are rendered difficult in many cases, especially when the permanent flow obscures the relatively small, superimposed elastic deformation. In a sense, asphalts may be regarded as imperfectly elastic fluids, the elastic and viscous deformations occurring simultaneously upon application of a shearing load. The elastic nature of certain types of hard, air-blown asphalts may be demonstrated visually and qualitatively by flexing a small bar of the material and observing the recovery after release of the pressure. The resilience, as well as an elastic fore-effect, has been observed in a large variety of asphalts during the course of numerous experiments performed at low shearing stresses in a conicylindrical rotation viscometer.[2] It was possible to evaluate the resilience for comparative purposes by determining the recovery

* The preceding three papers in the series will be found in Physics **5**, 221–4 (1934); **6**, 58–60 (1935); and **7**, 67–72 (1936).

† Presented at the eighth annual meeting of the Society of Rheology, New York, N. Y. Oct. 31, 1936.

[1] R. N. Traxler and C. E. Coombs, J. Phys. Chem. **40**, 1133 (1936).

[2] M. Mooney and R. H. Ewart, Physics **5**, 350 (1934).

TABLE I. *Identification of asphalts.*

DESIGNATION	SOURCE	TYPE	PROCESS	PENETRATION 25°C 100 g, 5 sec.	R & B SOFTENING POINT (°C)
A	Venezuelan	Petroleum	Air-Blown	65	68.9
B	"	"	"	122	51.1
C	"	"	"	94	57.2
D	"	"	"	95	55.5
E	"	"	"	44	65.8

TABLE II. *Elastic return deformation of asphalt A at 25°C (after being sheared at 21,900 dynes/cm²).*

TIME OF OBSERVATION (minutes)	ELASTIC RETURN DEFORMATION (degrees)
0	0
1	0.2
60	1.2
1020	2.4
1560	2.6
2520	2.65
3960	2.7

(elastic return in degrees) either (1) after a given period of time had elapsed, e.g., one hour, or (2) after the rate of recovery had decreased below a fixed value which should be quite small. The latter method was used in the experiments to be described.

The source, method of processing and identifying properties of the various asphalts discussed in this paper are given in Table I.

An illustration of elastic fore- and after-effects is afforded by Fig. 1 where asphalt *A* was sheared at a mean shearing stress of 6530 dynes/cm² at 35°C in the conicylindrical rotation viscometer until a constant rate of rotation was obtained. The shearing load was then removed and the rotor began turning in the reverse direction of its own accord. The return movement was recorded until the rate of rotation was less than about 0.05° per 20 minutes.

At first the elastic deformation was considerable, causing the sample to appear less viscous than it actually was. However, after a sufficient period of working (110 minutes), the elastic movement was completely obscured by the viscous flow and a constant equilibrium viscosity was obtained. The sample was worked 60 minutes longer to assure the constancy of this viscosity value and the load was released. The rates of return movement were then recorded.

The effect of temperature on resilience is shown in Fig. 2 where "elastic return" measurements were made in the conicylindrical rotation viscometer on asphalt *A* at 25°, 35°, 45° and 55°C.

If the angles of return deformation are plotted against the mean shearing stresses acting in the sample before removal of the loads, the resulting curve is not linear, at least not under the conditions of measuring the return angle employed here. Furthermore, the data show that at any stress, the elastic return deformation is greater in the sample the higher the temperature. At first sight it might be concluded that the softer an asphalt becomes, due to a rise in temperature, the more elastic it is. Actually, this is not the case. In the field of flow in rubber and resins it has been found that the more

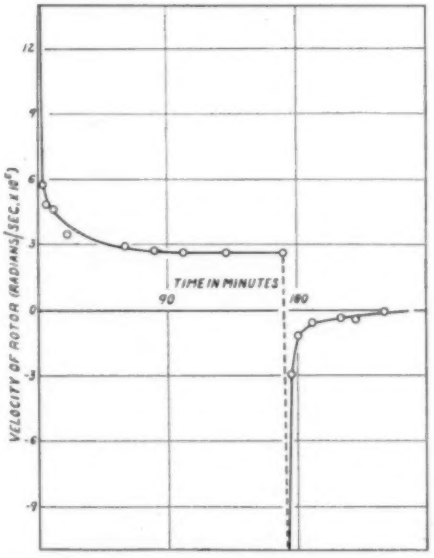

FIG. 1. Elastic effects in asphalt *A* at 35°C.

viscous an imperfectly elastic material is, the longer the period of time required for the attainment of its maximum recovery. In other words, the more fluid the material is, the more readily the structural elements within the substance are enabled to return to whatever arrangement they will ultimately assume by virtue of their elastic nature. In the case of asphalt we should therefore expect that the elastic return deformation of a soft asphalt over a small period of time would be more complete than the return of a hard asphalt during the same time interval.

To show that the resilience of a hard asphalt

is not at all complete at the end of one hour from the time of release of a shearing load, asphalt *A* was run at 25°C in the rotation viscometer at a mean shearing stress of 21,900 dynes/cm² until a constant velocity of the rotor was obtained. The load was removed and the elastic return was measured over a long period of time. These results are shown in Table II.

At 60 minutes the recovery is by no means complete. An evaluation of the elasticity of asphalt on the basis of the resilience over a short period of time might lead to erroneous conclusions since the recovery would be more complete in a fluid asphalt than in a more viscous one at any shearing stress.

Several years ago W. Braunbek investigated[3] the elastico-viscous effects of a bitumen-gutta-percha mixture called Chatterton compound in a rotation viscometer. He found that with continued working of the material at low shearing stresses the asymptotic approach of the rotor velocity to a constant value (on addition of a load) and the asymptotic approach of the reverse velocity to zero (on sudden unloading) are more or less reflected curve forms. Ordinarily, in air-blown asphalts a long period of time is required for the attainment of a constant rotor velocity since the elastic fore-effect diminishes very slowly. If Braunbek's concept held true for asphalts generally, the viscosities of highly elastic air-blown asphalts could be estimated quickly provided that the relation between return velocities and time remained the same no matter how soon after starting the experiment the loads were removed. A sample could be sheared for a few minutes in one direction, the load removed, and the reverse rotor velocities observed. The forward-minus-reverse velocities would equal the final constant rotor velocity from which the equilibrium viscosity is ordinarily calculated. A limited amount of experimental data has been analyzed by this method with varying degrees of success. Considerable work will be necessary before this procedure can be evaluated as a method for estimating the viscosities of the different kinds and consistencies of highly elastic asphalts.

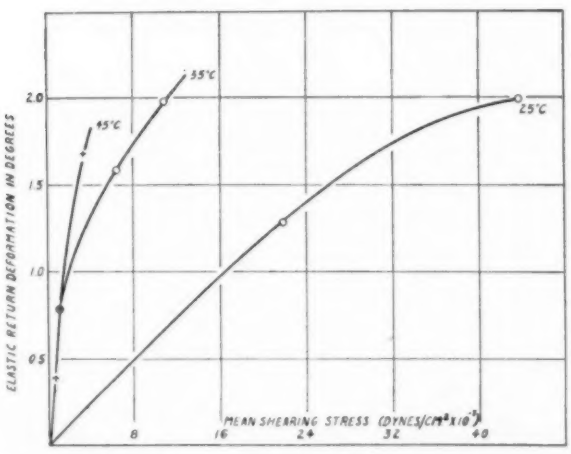

FIG. 2. Effect of temperature on resilience of asphalt *A*.

[3] W. Braunbek, Zeits. f. Physik **57**, 501 (1929).

THIXOTROPY

Using the conicylindrical rotation viscometer it has been found that above a particular "threshold" value of shearing stress (and rate of shear) which varies from asphalt to asphalt, thixotropy occurs in certain kinds of bitumen. Fig. 3 illustrates the type of data obtained.

The elastic fore-effect was overcome gradually just as in the case shown in Fig. 1, and the apparent viscosity increased; from 30 to 60 minutes the value was constant at 126×10^6 poises. Upon further working the "viscosity" of the sample decreased until it reached a final constant value of 83.8×10^6 poises between 615 and 805 minutes. The elastic return is of the same nature as the one shown in Fig. 1.

Another type of experiment showing the thixotropic behavior of asphalt is illustrated by the data in Table III.

Asphalt *B* was run in the rotation viscometer at 25°C under a small shearing load until the elastic fore-effect was obscured and the apparent viscosity became constant. A much higher load was then applied to the sample. The elastic fore-effect was very brief because after five minutes from the time of applying the load, a slow breakdown of structure occurred in the sample at the high rate of shear then effective, resulting in diminishing "viscosities." At 30 minutes the viscosity was still decreasing. The large load was removed and the original small one used again. Table III shows that the apparent viscosity was very small at the beginning of this test. However, despite the fact that

TABLE III. *Thixotropic behavior of asphalt B at 25°C.*

MEAN SHEARING STRESS (dynes/cm²)	TIME OF WORKING (min.)	RATE OF SHEAR (reciprocal sec. $\times 10^6$)	APPARENT VISCOSITY (poises $\times 10^{-6}$)
2,020	1	5.51	3.67
	5	4.83	4.19
	10	3.31	6.11
	30	2.89	6.99
	60	2.76	7.33
	80	2.76	7.33
	100	2.76	7.33
46,600	1	209	2.22
	5	161	2.89
	10	189	2.46
	20	208	2.24
	30	230	2.03
2,020	1	8.27	2.45
	5	6.90	2.93
	10	5.51	3.67
	30	4.42	4.58
	60	4.14	4.89
	190	3.31	6.11

the sample was being sheared, the structure formed again as indicated by the increasing "viscosities." At the end of 190 minutes when the experiment was ended, the apparent viscosity had reached a value of 6.11×10^6 poises, and was still increasing slowly. Had the experiment continued several hours longer, the original equilibrium "viscosity" (7.33×10^6 poises), obtained when the small load was applied to the sample the first time, would probably have been approximated.

Another aspect of thixotropic behavior is seen in the age-hardening phenomenon which occurs even in bitumens which are originally Newtonian. An asphalt which has been brought to a molten condition and then allowed to cool to a constant temperature (25°C) increases in viscosity very rapidly during the first hours of its life, and then continues to harden slowly. The extent and rate of age-hardening is most conveniently determined by measuring the viscosity of individual samples of an asphalt at definite time intervals. The technique of such experiments and the results obtained on a variety of asphalts of different source and type of processing have been described elsewhere.[4] The falling coaxial cylinder viscometer was found very convenient for these age-hardening experiments. The increase in viscosity with time is exhibited by air-blown asphalt *C*, as seen in Table IV.

[4] R. N. Traxler and H. E. Schweyer, A.S.T.M. **36**, II, 544 (1936).

This asphalt showed a very pronounced increase of viscosity with time; at the end of 1850 hours, a sample was remelted carefully and the viscosity reverted to approximately the original value (as shown by the values in parentheses at the end of Table IV). It was shown[4] in similar fashion from the work on a large number of asphalts that the amount of permanent hardening due to volatilization or chemical reaction is small in comparison with the increase in viscosity due to the structure which develops with time and which may be readily destroyed by heat. In general, air-blown asphalts show greater rates of age-hardening than steam or vacuum-refined asphalts.

The viscosity of an aged asphalt may be reduced by mechanical working as well as by heating, again indicating that the aging phenomenon is chiefly thixotropic. A sample of

TABLE IV. *Age-hardening of asphalt C at 25°C.*

TIME (hours)	APPARENT VISCOSITY (poises $\times 10^{-6}$)
4	12.3
26	15.1
52	16.3
100	18.8
171	21.7
700	31.4
1850	41.9
(3)	(11.4)

asphalt *D* was run at 25°C in the conicylindrical rotation viscometer at an age of 2 hours. The equilibrium "viscosity" was obtained and the sample permitted to stand undisturbed at 25°C. At an age of about 70 hours, the viscosity was determined at the same shearing stress used previously. The sample was definitely more viscous at the end of 70 hours as may be seen from Fig. 4, but with continued working the equilibrium "viscosity" was the same as that obtained when the sample age was 2 hours.

The elastic fore-effect was present when the sample was 2 hours old, but there was only slight evidence of thixotropic behavior. At the end of 70 hours, however, both effects were quite marked. In the former case, an equilibrium "viscosity" was obtained after about 75 minutes, in the latter case about 260 minutes of working were required for the attainment of the same constant value.

Non-Newtonian Flow

Although many asphalts have the appearance of being solid, no evidence has been found suggesting the presence of a "yield value" in any of the asphalts so far studied even though very low shearing loads have been employed in many cases. Some workers have found it convenient to classify materials as being plastic if the flow deviates in any respect from truly viscous behavior. Less confusion would result if the term "plasticity" were reserved for cases where "yield values" are known to occur. As has been suggested many times in the literature, such terms as non-Newtonian flow, quasi-viscousness, or "apparent viscosity" may be used in the case of materials where the curve showing the relation between shearing stress and rate of shear is not linear. A typical example of non-Newtonian flow in asphalt is given in Table V where asphalt *E* was run in the conicylindrical rotation viscometer at several mean shearing stresses. The apparent viscosity decreased with increasing shearing stress, and the plotting of rate of shear *vs.* mean shearing stress resulted in a curvilinear relation, the curve passing through the origin. No thixotropic tendency was observed at these low shearing stresses. The "viscosities" are equilibrium values deduced from the stationary rotor velocities after the elastic fore-effects had become negligible.

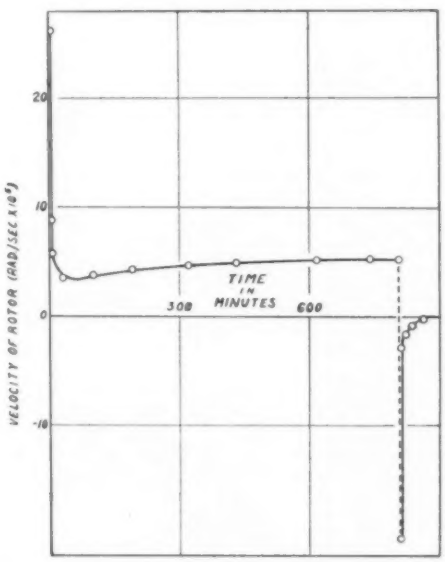

Fig. 3. Elastic and thixotropic effects in asphalt *A* at 25°C using the conicylindrical rotation viscometer (mean shearing tress = 41,700 dynes/cm²).

Correlation of Viscosity Values Obtained by Different Types of Viscometers

It is important to remember that asphalts cannot be classified broadly either as viscous or anomalous systems regarding their nature of flow. As stated previously, the existence and magnitude of the anomalous flow characteristics depend not only on the type of bitumen, but also on the temperature and rates of shear at which the measurements are made, and on the method and degree of processing to which the asphalt has been subjected.

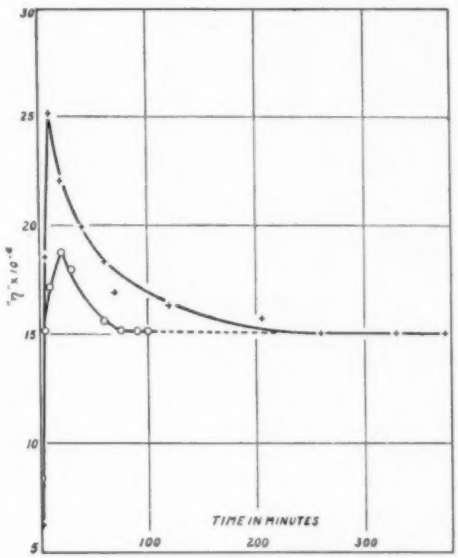

Fig. 4. Effect of mechanical working on the age-hardening of asphalt *D* at 25°C.

In our laboratory four kinds of viscometer have been used successfully for measuring the absolute viscosities of highly viscous asphalts: (1) a modified Bingham-Murray capillary tube plastometer, (2) the Bingham-Stephens alternating stress viscometer, (3) the coaxial falling cylinder viscometer (after Segel and Pochettino), and (4) the conicylindrical rotation viscometer (after Mooney and Ewart). A description of the dimensions and features of these instruments, as well as the technique employed in their operation at our laboratory, are given elsewhere.[5]

[5] R. N. Traxler and H. E. Schweyer, A.S.T.M. **36**, II, 518 (1936).

TABLE V. *Non-Newtonian flow of asphalt E at 25°C.*

MEAN SHEARING STRESS (dynes/cm²)	MEAN RATE OF SHEAR (reciprocal sec. $\times 10^6$) at equilibrium	APPARENT VISCOSITY (poises $\times 10^{-5}$) at equilibrium
891	0.339	2.63
6370	3.15	2.02
32300	19.3	1.68

Although no extensive correlation has been undertaken regarding the comparison of the "viscosities" of air-blown asphalts as measured by the various types of viscometer, some interesting observations have been made on a large number of steam and vacuum-refined asphalts which have a direct bearing on results obtained from air-blown asphalts.

A number of experiments were performed to see whether the viscosities obtained by the different methods were in agreement. Each asphalt was run at approximately equal mean shearing stresses in every instrument;[6] all samples were poured simultaneously, cooled, and aged alike.

The results showed a close agreement in the case of asphalts which did not depart appreciably from viscous flow. This behavior indicated that for viscous materials, the theories and equations of the various instruments were valid. When, however, asphalts were used which displayed anomalous flow properties, the discrepancies between the values obtained by the respective viscometers became greater as the magnitude of the anomalous characteristics increased. In such cases, the coaxial falling cylinder viscometer always gave the lowest results, and generally, but not always, the values obtained by the conicylindrical rotation viscometer were higher than those of the other methods.

Several experiments and analyses of data have been undertaken in order to determine what factors contribute most to the discrepancies in the viscosity values obtained by the various viscometers. As yet, however, the study is not complete enough to warrant any assertions.

[6] For convenience the Bingham-Murray apparatus was used only for asphalts under approximately 10^6 poises, the Bingham-Stephens viscometer for asphalts above this value. The limits of either of these instruments are not indicated by this choice.

Probably the most audacious task the human mind ever undertakes is attempting to predict what the human mind will ultimately accomplish. This is particularly true of attempting to predict what will be done by inventors—those peculiar but invaluable individuals whose principal assets are a healthy dissatisfaction with things as they are, and an incurable optimism as to the possibilities of improvement. However, history has shown and I think that even the pessimistic prophets of the past, were they living today, would concede that the only gross error which could be made in such a prediction would be to underestimate the infinite possibilities of the human mind in the fields of research and invention.

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CURRENT LITERATURE OF PHYSICS

THE Editors present for convenient reference in this section a list of those articles dealing with physics published in some thirty selected journals. Their definition of the scope of physics and their selection of the particular journals to be included are necessarily based on their interpretation of the wishes of the majority of the readers. The emphasis is placed on prompt mention and convenience of use rather than completeness. For many other excellent articles and publications, reference should be made to the regular abstract journals. Miss Margaret Shields, Physics Librarian at Princeton University, very kindly prepares the listings for the foreign language journals.

American Physics Teacher

VOL. 5, NO. 1, FEBRUARY, 1937.

Models to Illustrate Gyromagnetic and Electron-Inertia Effects. pp. 1–6. ***S. J. Barnett***

Principles Involved in Determining the Absolute Values of the Electrical Units. pp. 7–14. ***Harvey L. Curtis***

Training of Physicists for Industrial Positions. pp. 14–21. ***A. R. Olpin***

Some Fallacies in Textbooks on Modern Physics. pp. 22–25. ***Gordon Ferrie Hull***

Proposal for a Comprehensive Examination in Physics at the Baccalaureate Level. pp. 25–26. ***C. J. Lapp***

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First Lectures in College Physics. pp. 29–30 ***Alfred H. Weber***

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Annalen der Physik

SERIES 5, VOL. 28, NO. 4, JANUARY 16, 1937.

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Heat Conduction in Rarified Gases. pp. 319–324. ***E. Fredlund***

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Transverse Vibration of Parallelogram Plates with Free Edges. pp. 353–360. ***B. Pavlik***

Diffusion of Heavy and Light Hydrogen Through Argon. pp. 361–374. ***F. Wolf***

Dependence of Magnetic After Effect On Internal Potentials. pp. 375–384. ***H. Kindler***

Annales de physique

SERIES 11, VOL. 7, FEBRUARY, 1937.

Black and White Fringes on Radiographs (Mach Effect). pp. 141–229. ***B. Demetrovic***

Magnetic Double Refraction of Solutions of Salts of Rare Earths. pp. 230–290. ***C. Haenny***

Astrophysical Journal

VOL. 85, NO. 2, MARCH, 1937.

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Hydrogen Emission in the Chromosphere. pp. 88–106. ***D. H. Menzel and G. G. Cillié***

Illumination of Reflection Nebulae. pp. 107–138. ***L. G. Henyey***

Canadian Journal of Research

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Note on the Eupatheoscope and the Measurement of Equivalent Temperature in Canada. pp. 25–33. ***C. D. Niven***

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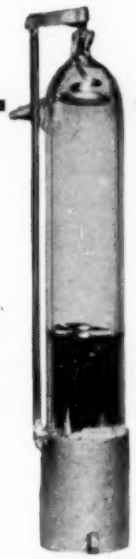

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Journal of the Optical Society of America

VOL. 27, NO. 2, FEBRUARY, 1937.

New Method for the Determination of the Transmission Factor of a Spectroradiometer. pp. 65–68. ***K. K. Kay and H. M. Barrett***

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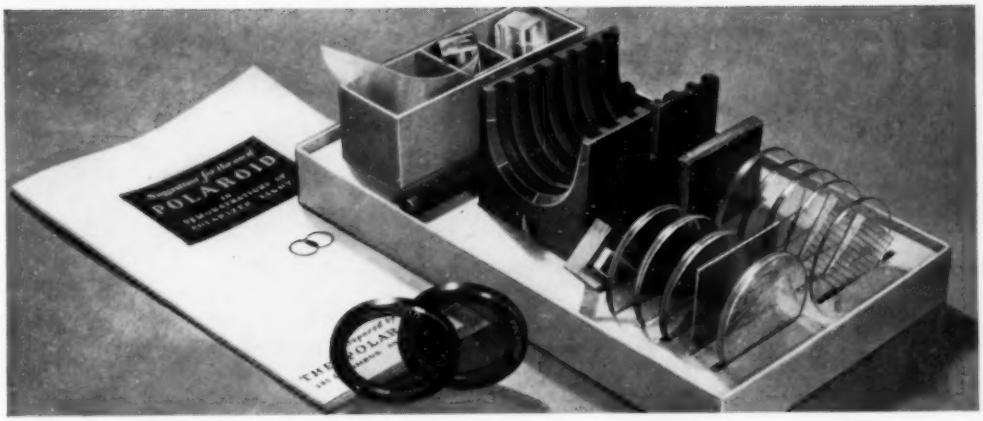

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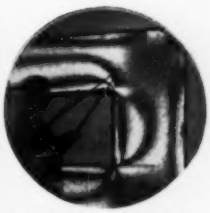

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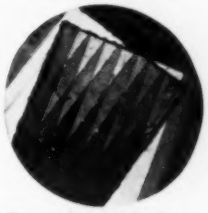

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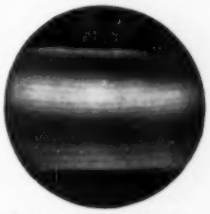

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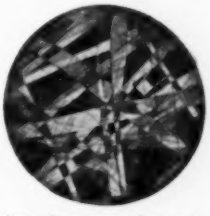

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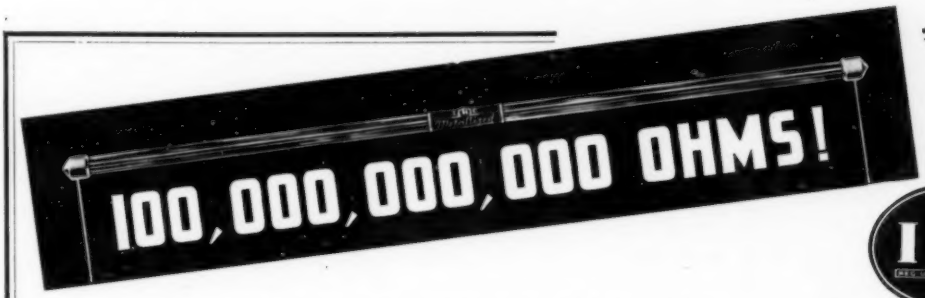

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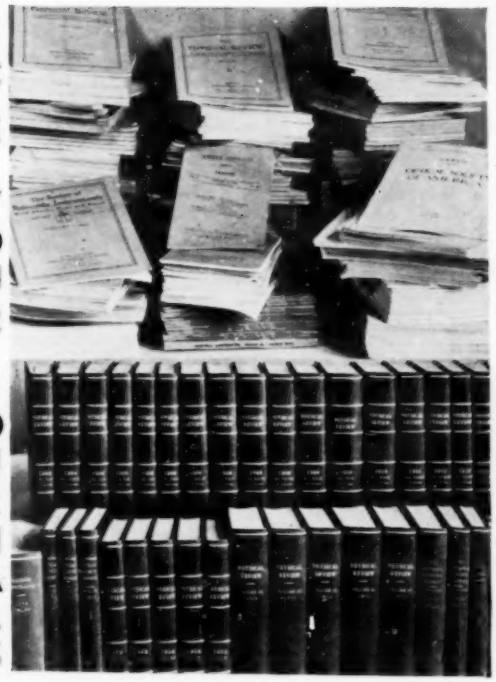

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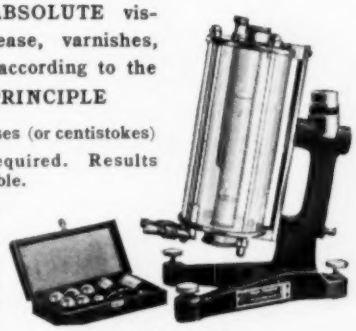

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